AN ELEMENTARY

TEXT-BOOK OF CHEMISTRY.

BY

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BY

WILLIAM G. MIXTER.

PREFACE.

THIS work is designed for use in schools and colleges. The aim is to present the elements of chemistry logically as far as possible, so that the student may grasp the fundamental principles of the science, and at the same time learn something of the chemistry of common things.

With this aim in view the Periodic Classification has been adopted. The acidic and basic groups are treated alternately in order to discuss bases and salts early in the course, as well as to give constant variety to the character of the experiments performed. Compounds of the rare elements are described to make evident the reasons for the classification, and also to serve as a basis for the summaries of the groups. The descriptions of the rare elements and their compounds, and of the less important compounds of the common elements, are in small type.

Graphic and constitutional formulas are much used, since they better represent the properties of compounds than empirical formulas, and also because they facilitate the study of inorganic as well as organic chemistry. The reasons for a number of constitutional formulas are given, and in case of compounds whose constitution is not understood, care is generally taken to state that the constitutional formulas employed are assumed from analogy. While graphic formulas are very constantly used for common substances for the sake of rendering such formulas familiar, it is not intended to imply that the use of empirical formulas should be avoided.

What to teach beginners in chemistry, and how best to do it, are difficult questions. Most students are interested in the subject, and study faithfully and enthusiastically, needing only guidance and instruction. It is the duty of the teacher to help them to think for themselves, to aid in drawing conclusions from experimental data, and to make sure that they understand the reasons for the fundamental theories. Experience shows that the student is apt to retain a general knowledge of the philosophy of chemistry far better than a specific knowledge of substances; nevertheless, knowledge of many compounds is necessary to the discussion and comprehension of theories. The work in the laboratory yields this knowledge most readily, and at the same time trains the powers of observation.

Numerical data, though essential in descriptions of substances, should not as a rule be required for recitation. A table of atomic weights, hung in the class-room, will remove the temptation to memorize atomic weights. Such a table, which can be best exhibited in the form of the periodic classification, will early render familiar the groups of the elements, and be of service in many other ways. It is recommended, in assigning a lesson, to point out the portions requiring special attention and also those parts of the text which may be omitted. The difference in type used will aid the teacher in his selections, but some of the text in large type may properly be regarded as matter for reading rather than for recitation. The instructor should emphasize the fact that the members of a group form analogous compounds with other elements.

It is preferable to have the work in the laboratory, as far as practicable, precede the recitation on a topic. The students can then more readily understand the statements contained in the text. Questions on the laboratory work and a discussion of the results of experiments are perhaps of more value than questions on the text. At the beginning of the

course all experiments should be made before the class, and detailed directions given for those to be made by the students. Afterwards it will be better to have them depend more upon the results derived from their own experiments. Constant supervision of laboratory work and aid in manipulation are necessary, but the student should be left to obtain results, the suggestions coming from the teacher rather in the form of questions. Reference should be made during the laboratory work to the text-book for information about substances and reactions.

The author acknowledges with pleasure the valuable aid his colleagues have generously given him in the preparation of this book. Professor Wm. H. Brewer, who has for many years given instruction in the laboratory to beginners, has made many suggestions about experiments and methods of teaching. Professor Charles S. Hastings has supplied the part on Physics of Chemistry and Spectral Analysis, and given assistance on portions of the proof. Professor R. H. Chittenden read most of the manuscript and made many suggestions. Professor H. L. Wells read the part on iron and steel.

SHEFFIELD LABORATORY OF YALE UNIVERSITY,
      NEW HAVEN, December, 1888.

CONTENTS.

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PHYSICS OF CHEMISTRY.

Fundamental Conceptions.

Physical Magnitudes.—There are three fundamental conceptions of quantity which furnish the means for measuring all magnitudes involved in physical science, namely, of space, of time, and of matter. Our ideas, whether innate or derived from experience, are sufficiently precise concerning the first two quantities to enable us to presume a sufficient knowledge of their natures for all practical purposes; the last, however, requires more particular consideration.

Matter.—The existence of matter, and of matter alone, is demonstrated to us by the direct evidence of our senses. We infer the existence of forces, of electricity, etc., by observation of changes going on in matter, but we have no sense-organs which betray the existence of any of them to the mind directly. For the discussion of purely chemical phenomena we may define matter as anything which can be weighed, and the quantity of matter as proportional to its weight.

The one essential property of matter from the chemical standpoint is its indestructibility. From this property, which forms the logical foundation of the science of chemistry, we may deduce the practical rule:

In any closed space the total quantity of matter is invariable, irrespective of the changes of form which it may undergo.

For example, if we have a closed vessel containing a quantity of ice, we may by heating it convert it first into water,

then into steam, then into its component gases, hydrogen and oxygen, and then, probably, into simpler forms of these elements; but with all these changes the total quantity of matter remains unchanged.

Fundamental Units.—The unit of length now almost universally employed in science is the centimeter (equals 10 millimeters), and is the unit which we adopt.

The unit of time is the second.

The unit quantity of matter, or unit of mass, is a quantity of matter equivalent to that contained in a cubic centimeter of water at its maximum density. It is called a gram.

Derived Units.—As has already been noted in the first paragraph, all quantities measured in physical science can be expressed in terms of these three fundamental units. For example, an area is expressed in terms of the unit of length squared, that is, in square centimeters: a velocity, in terms of the unit of length divided by the unit of time; as, for example, a velocity of ten, means a change of place at the rate of ten centimeters per second, etc. These are examples of derived units.

Among the most important derived units employed in chemistry are:

1° *Density.*—This is defined as the quantity of matter divided by the space it occupies. Since the definition of unit quantity of matter tells us that in a body of water the number of units of mass is equal to the number of cubic centimeters it occupies, the density of water is unity. As experiment shows that a given bulk of mercury contains 13.6 times as much matter as an equal bulk of water, the density of mercury is 13.6.

It is obvious that these values depend upon the arbitrary condition that a unit volume of *water* shall contain a unit of matter. In the English system of units, if we take the cubic

foot as the unit of volume and the pound as the unit of mass, the density of water (since a cubic foot contains 62.5 pounds of matter) is 62.5. In any system, however, the *ratios* of the densities are the same; hence, as the density is very characteristic of liquids and solids, these ratios taken with respect to water are made to replace the inconvenient densities in systems other than the metric. Such ratios are called *specific gravities*: they are obviously numerically equal to the densities in the metric system. As the last-named system is adopted in this book, the term has no place in it.

2° *Motion.*—A quantity of motion is equal to the product of the mass of a moving body by its velocity. Thus, the motion of a kilogram of matter moving one centimeter per second is equal to the quantity of motion of a gram moving a thousand centimeters per second, which is equal to a thousand units of motion.

3° *Force.*—The cause of change of motion is called *force*, and its measure is the rate at which it can produce the change. A unit force is, therefore, a force which can increase the velocity of motion of a gram one centimeter per second, or the velocity of motion of a kilogram one one-thousandth of a centimeter per second. It is called a *dyne*. If a gram of matter be allowed to fall freely, it is found that its velocity increases at the rate of 980 centimeters per second, hence the *weight* of a gram is 980 dynes.

4° *Pressure.*—A force may be applied at such a small portion of the surface of a body that this portion may conveniently be regarded as a point; for example, when a moving billiard-ball strikes another, the surface of contact is always small during the whole duration of the action. In other cases, however, the surface directly acted upon may be large, as in the case of a vessel driven by sails. In this second case it is often convenient to know how much force is applied to each unit of area. This is found by dividing the whole force by the area over which it is distributed, and the result-

ing magnitude is called the *pressure*. The unit of pressure
obtains when a force of one dyne is distributed over each
square centimeter of area.

Practical Units.—Although the system defined above is the
simplest and most convenient for all exact calculations, and
even understanding of complex physical phenomena, it has
the disadvantage of being in some of its features quite remote
from our ordinary experience.   Hence, although it has made
its way into the science of physics among all nations, in those
branches of physical science where only comparatively simple
conceptions of magnitude, or ratios of magnitudes, are dealt
with, the need of a logically consistent system of units has not
been felt.   Thus in chemistry, although the rigidly scientific
system has much to recommend it, its introduction here would
necessitate so great a change in chemical terminology that the
loss would be more than the gain.   Therefore, although the
units as defined up to, and including, density are used in
this text-book, the units of force and pressure, in accordance
with ordinary usage, are defined otherwise.

All bodies are attracted towards the earth in the direction
of the plumb-line.   This particular manifestation of force is
called *weight,* and for the same body it is found to be nearly
the same all over the world.*

Thus the weight of one gram of matter may be taken as the
unit of force.   The great objection to this definition is that
the term " gram weight " has two very distinct meanings: it
may mean a unit by which we measure quantities of matter, or,
a unit (not perfectly definite) by which we measure quantities
of force.   It is in the former sense that it is generally used,
and always in this book unless specifically excepted.

Instead of defining pressure in terms of this new unit of
force, namely, a " gram weight " per square centimeter, chem-

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* The total variation is about one half of one per cent.

ists are accustomed to take a unit 13.6 times as large, that is, the weight of a cubic centimeter of mercury divided by a square centimeter. This practice has grown up from the almost universal use of mercury as a means for measuring fluid pressures, not only in the barometer for measuring the pressure of the atmosphere, but also in other forms of manometers. This practice has also fixed the habit of designating pressures by lengths; thus, a pressure of 76 cm. or 760 mm. means a pressure equal to that due to the weight of mercury at a surface 76 cm. below the free surface of a vessel of mercury. To reduce it to grams weight per square centimeter, we must multiply the number indicating the length in centimeters by 13.6, the weight in grams of a cubic centimeter of mercury. Since nearly all problems in chemistry have to do with ratios of pressures only, and the ratios of the lengths of the measuring columns of mercury are the same as those of the absolute pressures, this process of reduction is rarely necessary.

Forms of Matter.

Matter appears to us in various forms, which, however, can all be reduced to two classes, namely, solids and fluids.

A Solid is a body which offers resistance both to change of shape and to change of bulk.

A Fluid is a body which offers no resistance to change of shape.

Fluids, again, can be divided into two distinct types: liquids and aeriform bodies.

Liquids are those fluids which resist forces tending to in-

crease their bulk as well as those tending to diminish it.   On account of this tendency of a liquid to keep its volume unchanged, it is possible to keep a vessel partly full of a liquid, in which case the liquid will be bounded by one or more *free* surfaces, i.e., surfaces which separate it from an aeriform body.   Water is the most familiar example of a liquid.   By experiment it has been found that a pressure of one atmosphere (equals 76×13.6 grams weight per square centimeter) will reduce its volume one twenty-thousandth part only.   On the other hand, it will resist a force at least ten times as great as this which increases its bulk before breaking—a strength doubtless greater than that of many friable solids.

Aeriform Bodies are those which oppose resistance to forces tending to diminish their bulk, but none whatever to a force tending to increase it.   For this reason it is impossible to have a vessel partially filled with an aeriform body, the remainder being empty.   Nor, since all aeriform bodies are perfectly miscible, is it possible for an aeriform body to have a free surface, i.e., to be self-bounded.   Another convenient distinction between liquid and aeriform fluids, depending on the possibility of a free surface, is this:—a liquid can be poured in drops, but an aeriform fluid cannot.

Gases and Vapors.—Certain aeriform bodies, such as air, hydrogen, oxygen, etc., at ordinary temperatures, are subject to a very simple law known as Boyle's law, namely, that if the temperature remain unchanged the product of the pressure and volume is constant.   Such bodies are called *gases*.   If the aeriform body does not follow this law it is called a *vapor*. We have then the following definitions:

A gas is an aeriform fluid in which the product of the pressure by the volume is constant at a constant temperature.

A vapor is an aeriform fluid in which, at a constant temperature, this product is not constant.

It is important to note that experiment proves that every vapor becomes a gas at a sufficiently high temperature and low pressure, and, conversely, every gas becomes a vapor at sufficiently low temperature and high pressure. For example, steam at a pressure of 76 cm. and a temperature of 200° C., or at a pressure of 0.1 cm. and a temperature of 20° C., may be regarded as a gas; while carbon dioxide is distinctly a vapor at a temperature of 30° C., if the pressure be 60 or 70 times as great as that of the atmosphere.

It may be useful to recapitulate the different forms of matter with which we have to deal in the science of chemistry. They are:

I. Solids.

II. Fluids. $\begin{cases} \text{Liquids.} \\ \text{Aeriform bodies.} \begin{cases} \text{Gases.} \\ \text{Vapors.} \end{cases} \end{cases}$

The Balance.

Sir Isaac Newton demonstrated that every body is attracted towards the earth by a force dependent directly upon the quantity of matter in it, or, in other words, that the weights of all bodies are directly proportional to their quantities of matter. A balance is an instrument for determining equality of weights. It consists of a light rigid beam supported so as to turn easily in a vertical plane about its middle point. To each end of the beam is suspended a pan, the two being so adjusted that when unloaded the beam remains horizontal; the position of the beam is determined by a pointer attached to it and moving over a graduated plate. If precisely equal masses are placed in each pan the tendency for each to descend is equal, and the beam remains horizontal; but if one of the

masses is greater than the other, that pan in which it is placed, on account of its greater weight, will sink.   If, then, we have a set of standard masses (*called weights*) and a balance, we may determine the quantity of matter in a body up to the value of the sum of the standard masses, and to a degree of accuracy limited only by the delicacy of the balance.   The process of determining masses is called weighing.
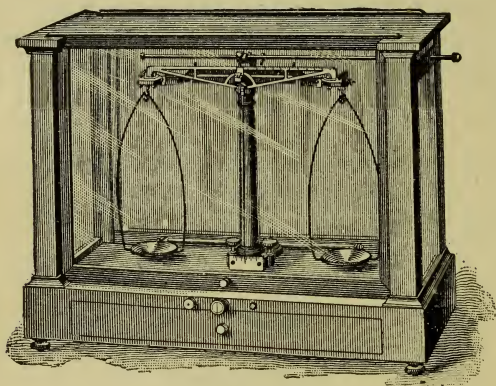
FIG. 1.

A form of balance extensively used is illustrated in Fig. 1. It is enclosed in a glazed case so as to protect it from currents of air when in use and from dust at all times.   Besides the essential elements already described, the instrument is provided with an arrangement by which the beam can be lifted from the delicate knife-edges upon which it is supported, so that, when not in use, they are not subject to wear.   A portion of this mechanism can be seen in the figure under the ends of the beam: it is actuated by the large knob in front of the base of the supporting column.   Another important accessory is the rod at the top of the case which projects through it at the right.   By means of this a small bent wire

can be placed upon the beam at a distance from its centre
read from the graduation of the beam. This wire is called a
rider, and it serves instead of a series of small weights which
would be inconvenient to handle.

Determination of Densities.—From the definition of density
it is only necessary, in order to find it for a given substance,
to find the mass of a known volume of the substance; then
the density is equal to the mass as determined by the balance,
divided by the volume.

For fluids, the process of determining density is of the
utmost simplicity. Suppose that we have a thin
flask, such as is illustrated in Fig. 2, so con-
structed that when the stopper is in place the
contents is exactly 100 cc. This condition may
be brought about by having the glass stopper
enter the flask so far that the cubic contents is
slightly too small, and then grinding away the
lower end until it is found to contain exactly
100 grams of cold water. In order to render
complete filling easy, the stopper has ordinarily
a fine capillary opening along its axis, and the
excess of liquid is removed by a bit of filter
paper so that the surface corresponds to a mark
on the stem. If now, such a flask be placed

FIG. 2.

empty on one pan of the balance and counterpoised, then
filled with the fluid whose density is desired and again
balanced, the added weights will measure the mass of 100
cc. of the fluid, and the density is, if m is the value of the
added weights, $\frac{m}{100 \text{ cc.}}$

EXAMPLE: A flask of 100 cc. capacity was counterpoised on the
balance; when filled with alcohol it required added weights equal to 80.95
grams for equilibrium. From these data we deduce 0.8095 as the

density of alcohol, i.e., each cc. of alcohol contains 0.8095 of a gram of matter.

The density of a gas is determined in a precisely similar manner, although, on account of the relatively small density of gases, certain precautions must be taken. For example, a flask containing much more than 100 cc. must be employed so that its mass may not be too large relatively to that of its contents. Again, in this case, when we weigh the flask empty, it must be truly void of air as well as all else—a refinement which is not essential in tolerably accurate determinations of densities of liquids.

Thus, Regnault found that a certain glass vessel, by determining the mass of water which would completely fill it, contained 9881.27 cc. He found also, that when the vessel was filled with dry air at a temperature 0° C. and under a pressure of 76 cm. it weighed 12.77827 grams more than when quite empty; hence the density of air under the conditions given is $\frac{12.77827}{9881.27} = 0.00129318 = \frac{1}{773}$ nearly. This is the classical determination of the important constant, and is the value at present accepted as the best attainable. The convenient vulgar fraction represents the decimal to within less than one part in two thousand.

For solids we must in general take a more indirect way for determining their densities. Of course if we have a solid body of definite shape and known dimensions—a sphere or a cube, for instance—we might readily calculate its volume, and then we should only require to determine the mass, and proceed as before. But as such a condition of regularity of shape would rarely occur in practice, we make use of a principle discovered by Archimedes, and known as the

Principle of Archimedes.—Suppose that we have a vessel of water at rest; imagine any sort of closed surface wholly within

the water, as represented in Fig. 3, separating one portion from the rest. It is clear that the water outside of the closed surface presses upon that within in such a way as to keep it in equilibrium, i.e., so that the total effect of the pressure from without is to sustain the weight of the body of water within. Now if the water within the imaginary surface be replaced by

Fig. 3.

any other substance, it is manifest that the pressure of the water outside would not be modified, and that the resultant pressure would still be as before, namely, equal and opposite to the weight of the volume of water previously enclosed. Hence the principle may be stated :
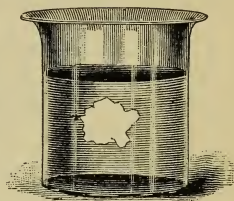
If a body be immersed in a fluid at rest, it loses a portion of its weight equal to the weight of its own bulk of the fluid.

The determination of the density of a solid by means of this principle becomes easy. The process is as follows :

Weigh the body in air, then in water; the difference of these two weights is the mass of its own bulk of water: divide the weight in air by the difference of the two weights and the quotient is the ratio of the density of the substance to that of water.

EXAMPLE : A piece of lead was found to weigh 325 grams in air, and 296.2 grams in water; hence the loss of weight was 28.8 grams, the ratio of its density to that of water $\frac{325}{28.8}$ or 11.3.

Frequently in chemistry we wish to determine the density of a substance—a salt, for example—which cannot be weighed in water on account of loss by solution. We may then perform the same operation with some other fluid which does not dissolve the substance. The reduction, as above, will yield the ratio of the density of the substance to that of the fluid

chosen, which, multiplied by the density of the fluid, gives the density of the material.

EXAMPLE: A piece of common salt was found to weigh 172.3 grams in air, and 107.2 grams in alcohol, of which the density has been found to be 0.8095. Consequently the ratio of the density of the salt to that of the alcohol is $\frac{172.3}{65.1} = 2.647$, and the absolute density 0.8095 times as great, that is, 2.143.

Crystallography.

Only a small portion of the solids brought to the attention of the chemist are of that simple character which exhibits like properties in all directions with no tendency to assume definite geometrical forms. Such simple substances are called amorphous (i.e., without form). They may be exemplified by glass, resins, gums, etc.

The vast majority of solids, on the other hand, not only show marked differences in their physical properties according to the direction along which they are tested, but also a remarkable tendency to assume, in the process of forming, certain definite geometrical figures bounded by plane faces. As an example of physical properties depending upon direction we may mention selenite (calcium sulphate), which can be broken in three directions only, and with three differing degrees of readiness; or calcite (calcium carbonate), which will fracture with equal ease in three directions only, but if heated will expand in a certain direction and contract in all directions at right angles to it. Again, as an example of the tendency to assume definite geometrical forms, we may take common salt (sodium chloride), which, if allowed to solidify from an aqueous solution, will be found in cubes, or in figures which might be built up of cubes.

A substance which is characterized by such properties is

called a crystalline substance.   Besides the substances already named, we might give ice, most gems, alum, sulphur, sugar, etc., etc., as familiar examples of crystalline bodies.

A piece of crystalline substance formed by continuous and spontaneous growth (whether from solution, as salt from brine; from fusion, as ice from water; or from vapor, as in the case of snow crystals, is immaterial) is called a crystal.   The form of a crystal of a substance is generally so characteristic that it affords a very valuable means of identification.   Again, since the tendency to crystallize depends largely on the purity of the material, crystallization often serves as a means of testing the purity as well as a means of separation.   Thus an elementary knowledge of the classification of crystals is indispensable to the chemist.

In a discussion of the laws governing crystals it is important to observe at the outset that regularity in a crystal is of exceptional occurrence.   Certain sides may be less favorably situated for growth, as, for example, in a crystal lying upon one side, that side is obviously unfavorably situated; again, in a solution where the temperature is not constant we can hardly expect regularity of crystal formation.   The elements which are constant and characteristic are the angles between the bounding planes, and to a less degree the frequency of the occurrence of certain faces.

To make the meaning of the last paragraph clear, we may illustrate the first characteristic by the example of crystallized quartz.   Any crystal of quartz, whatever its color or shape, could not fail of recognition if it had a sufficient number and variety of faces, for, although a particular angle might be found in crystals of other substances, the combination of angles proper to quartz does not recur in any other substance. The importance of the occurrence of certain faces, the second characteristic of a variety of crystals, may be illustrated by racemic acid.   Of this substance there are two forms which have most interesting differences.   If we compare the crystals

of the two forms we find that each kind possesses faces not found on the other, though all the crystal angles are alike in the two cases.   This peculiarity is the only known method of separating the two varieties of the acid.

The study of the various forms presented by crystals both natural and artificial has shown that they may be most simply described by reference to certain fixed directions in the substance called axes.   All forms may thus be referred to one of six systems.   They are :

I. *Isometric*, in which there are three axes at right angles to each other, the properties of the substance being alike in the three directions.

II. *Tetragonal*, in which the properties along two axes at right angles to each other are alike, while those along the third, which is at right angles to each of the others, are different.

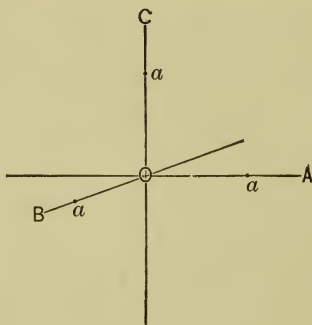III. *Orthorhombic*, in which again the axes are mutually

FIG. 4.

at right angles to each other, but the crystalline properties differ in all three directions.

IV. *Hexagonal*, characterized by four axes, three of which are in one plane equal and mutually inclined at an angle of

60°, while the fourth, or principal axis, is at right angles to the plane of the others.

V. *Monoclinic*, in which two of the axes are at right angles to each other, and the third, rectangular to one, is oblique to the other.

VI. *Triclinic*, in which all three axes are oblique to each other.

I. *Isometric.*—The fundamental principles of crystallography can be illustrated by a consideration of the simpler forms of the first class. Thus, in Fig. 4, let oA, oB, and oC be the directions of the three axes. Lay off on each equal distances from the centre, oa : then the law of crystals states, that any plane through the point a which either does not cut the other axes at all or cuts them at points a small multiple of the distance oa from o, determines the direction of a possible pair of faces in the crystal. Examples of forms so derived are given in Figs. 5 to 9.
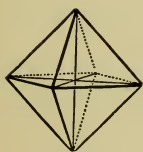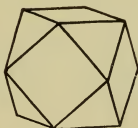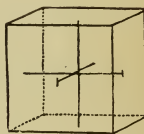
FIG. 5.   FIG. 6.   FIG. 7.   FIG. 8.   FIG. 9.

The first of the series is the regular octahedron : it is exemplified in crystals of alum and many diamonds. The last is the cube : examples are crystals of common salt, of fluor spar, of iron pyrites, etc. The intermediate forms, Figs. 6 to 8, inclusive, possess both octahedral and cubic faces.

The figures above only represent forms of which the determining planes either cut all the axes at equal distances, or cut one axis only. Obviously the system of planes next in geometrical simplicity are those which cut two axes only, and

those at equal distances. Figs. 10 to 14, inclusive, represent
derived forms having such planes, together with one or both
of the other systems, in a greater or less degree of develop-
ment. The first two of the series represent forms where
cubic faces and the third class of faces coexist, the cubic faces
being the more prominent in the first and the latter in the
second. Fig. 12 represents the form when the planes trun-
cating the edges of the cube have become so prominent that
the cubic faces wholly disappear; it is the geometrical figure
known as a regular dodecahedron, whence we may properly
call the faces dodecahedral faces. Crystals of garnet are
found of this form. Fig. 13 is a form in which all three sys-
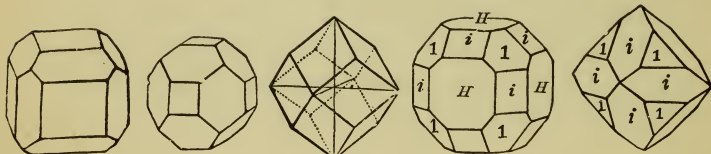
FIG. 10.   FIG. 11.   FIG. 12.   FIG. 13.   FIG. 14.

tems of faces are represented, namely, the octahedral 1, the
cubic H, and the dodecahedral i. Fig. 14 has only the octa-
hedral and dodecahedral faces.

When we consider that this considerable variety of forms is
derived from determining planes defined by their intercepts
on the axes, which vary only in the ratio of $1:1$ or $\infty:1$, and
that these ratios may be, according to the law of crystal for-
mation, equal to any number not large,* it becomes obvious
that the variety of possible forms in this one system is enor-
mously great.

One other characteristic of the isometric system should be
noted, as it distinguishes the first class from each of the oth-

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* A ratio larger than $9:1$ very rarely occurs.

ers. Inspection of Fig. 5 will show that nine planes can be passed through the centre, dividing the octahedron into symmetrical halves, namely, three defined by each pair of axes, and six planes, each of which passes through an axis, and bi-
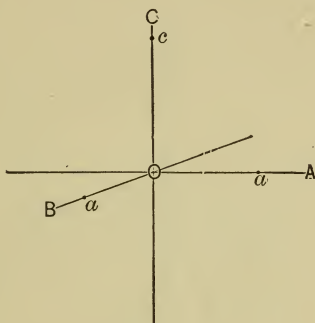
Fig. 15.

sects the angle between the other two axes. These nine planes will also divide all the other forms symmetrically; hence we say that the isometric system has nine planes of symmetry.

II. *Tetragonal System.*—The structure of this system may be elucidated by reference to the crystalline axes, Fig. 15. Here,
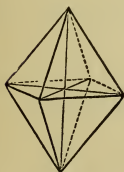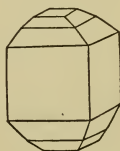
Fig. 16.   Fig. 17.   Fig. 18.   Fig. 19.   Fig. 20.

as before, the axes are mutually rectangular, but we must lay off on one axis, called the principal axis, a distance greater or less than the distance Oa, laid off on the other two. The

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ratio of *oc* to *oa*, for a given species of crystals must be found from a measurement of the angles between the proper faces. Having fixed these points, all that has been said concerning the derivation of crystalline forms in the first system is applicable here. Some of the forms are shown in Figs. 16, 17, 18,
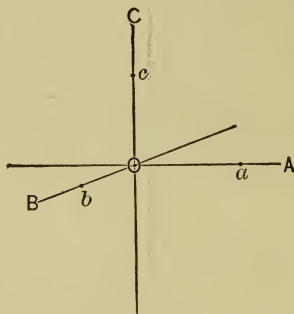
FIG. 21.

19, 20. Planes perpendicular to the principal axis are called basal planes. An example of a crystal in this system is zircon, often found of the form of Fig. 20.

The Tetragonal System has only five planes of symmetry. Inspection of Fig. 16 will make this clear.

III. *Orthorhombic System.*—Like the preceding, this is
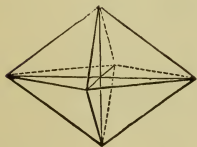
FIG. 22.   FIG. 23.   FIG. 24.

characterized by three axes at right angles to each other, all of which, however, are of unlike length, as in Fig. 21. The ra-

tios *oa* : *ob* : *oc* in general differ for each species of crystals, and can only be determined by measurement of the angles. Simple possible forms are represented in Figs. 22, 23, 24, 25, 26, 27.
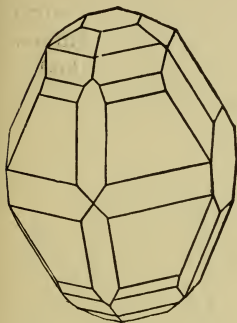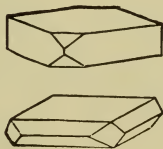
FIG. 25.   FIG. 26.   FIG. 27.

Familiar examples are Nitre and Aragonite (Fig. 27), Barites (Fig. 26), Sulphur (Fig. 25).
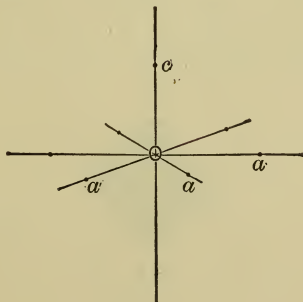
FIG. 28.

This system has three planes of symmetry only, namely, those defined by the axes taken two and two.

IV. *Hexagonal System.*—The characteristics of this system are most easily represented, at least geometrically, by reference to a system of four axes, three of which lie in one plane and are mutually inclined to each other at an angle of 60°, while the fourth, called the principal axis, is perpendicular to the plane of the others, Fig. 28. The three lateral axes are all equal *oa*, while the ratio of *oc* to *oa* is different for different species of crystals. Forms derived by the same methods of construction as before are shown in Figs. 29, 30, 31, 32, 33.

Fig. 29.   Fig. 30.   Fig. 31.   Fig. 32.   Fig. 33.
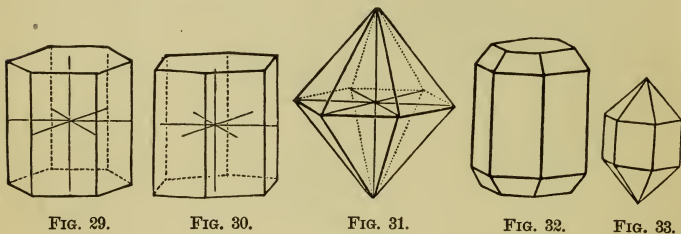
The planes perpendicular to the principal axis in Figs. 29, 30, 32 are called basal planes. In this system the octahedron does not occur, but if alternate faces of the double hexagonal pyramid Fig. 34 be suppressed, we have a form illustrated in Figs. 35, 36 which has, like the cube, only six sides, and is

Fig. 34.   Fig. 35.   Fig. 36.
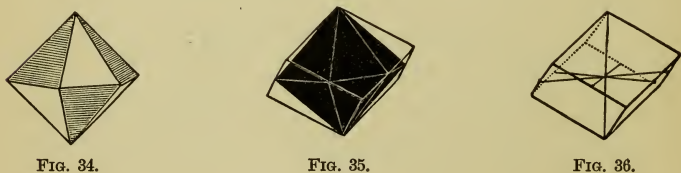
called a rhombohedron. Many of the hexagonal crystals—calcite for example—will cleave readily in planes parallel to these rhombohedral faces.

Examples of crystals of this system are corundum (occurring as Fig. 31), quartz (Fig. 33), and calcite (Fig. 36).

V. *Monoclinic System.*—The axial relations are indicated in Fig. 37. OA and OB are at right angles to each other, as are
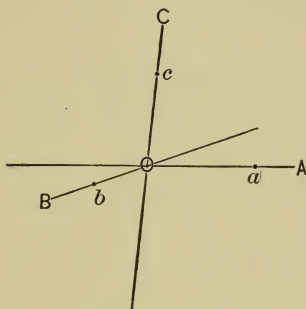
FIG. 37.

also OB and OC, but Oa and Oc are inclined. The ratios $oa : ob : oc$ may have any value except unity. Simple forms are illustrated in Figs. 38 and 39.
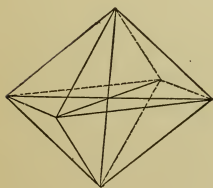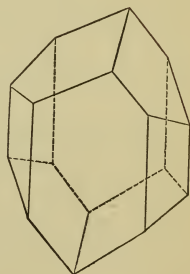
FIG. 38.   FIG. 39.   FIG. 40.

Examples of crystals of this system are feldspar (Fig. 40), and selenite (Fig. 39).

This system has only one plane of symmetry, namely, that of the axes OA and OC.

VI. *Triclinic System.*—This is characterized by three axes, no two of which are at right angles, and the axial ratios are all unequal. A crystal in this system has no plane of symmetry. The most familiar crystal of this system is that of copper sulphate.

Iso-, Di-, and Pleo-morphism.—Many chemical compounds of dissimilar but analogous composition present identical crystal forms. Such bodies are said to be *isomorphous*. As examples we may cite the various alums, which belong to the First System, and the calcite group, including calcite, dolomite, magnesite, etc., which belong to the Fourth System.

On the other hand, some substances are found to occur in crystals belonging to two or more of the six crystalline systems. If in two systems only, the substance is said to be dimorphous; if in more than two, pleomorphous. A good example of a dimorphous substance is sulphur, which, when crystallized from the liquid condition, forms crystals belonging to the Fifth System, but when deposited from solutions or from the vaporous state forms crystals of the Third System. Calcium carbonate is another common example. The substance is known under the names calcite, in which form it belongs to the Fourth System; and aragonite, the crystals being orthorhombic.

Molecular Structure of Matter.—In the study of crystals, by far the most important fact discovered is that the ratios for the interceps on the axes for a possible crystalline face are always rational, as defined in the law on p. 15. To interpret its physical meaning, let OA and OB (Fig. 41) be two axes of a crystal, and Oa_1, Ob_1 represent the interceps of that plane parallel to the third axis, which is found to bear the simplest relations to all other observed planes parallel to the third axis; then the law says that any plane passing through a_1 and

b_2, a_1 and b_3, a_1 and b_4, etc., or a_2 and b_1, a_3 and b_1, and a_4 and b_1, etc., are possible faces of a crystal, but no others can be. But if the material of the crystal were absolutely uniformly distributed, there is no assignable reason why a plane other than the ones thus defined should not occur. Hence we are obliged to conclude that the matter is arranged in isolated particles similarly to the arrangement of the dots in the figure. With this hypothesis as to the arrangement of the matter, it is easy to see what the crystallographic law means. The plane a_1 b_1 contains every particle of matter in its own direction, the planes a_1b_2 and a_2b_1 every second particle, etc., etc. This structure, so definitely indicated by crystals, is
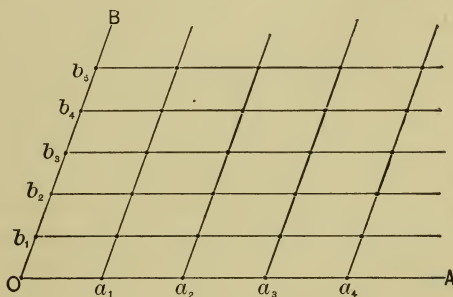
FIG 41.

called a molecular structure, and the particles are called molecules. Beyond this, crystallography teaches us nothing, except that structure must be exceedingly fine-grained, for in some cases perfectly polished planes containing every fifteenth row of molecules have been observed; but if this distance were any considerable part of a wave-length of light, i.e., about $\frac{1}{2000}$ mm., the polish could not be perfect: whence we conclude from such phenomena alone that there cannot be less than fifteen hundred thousand molecules side by side in the length of an inch. We shall find more accurate methods of indicating their distances and sizes further on.

Temperature and Heat.

Difference of Temperature.—When two bodies are brought into contact we find in general that one of them becomes cooler and the other warmer. The body which becomes cooler is said to be at a higher temperature than the other, and, other things being equal, we define the difference of temperature as proportional to the rate at which the process goes on. Equality of temperature obtains when neither of the bodies becomes warmer or cooler.

To measure differences of temperature we must take two substances having constant differences of temperature and give numerical values to each. For example, it is found that the difference in temperature between melting ice (or freezing water) and water boiling under a fixed pressure is constant; hence, if we call the temperature of melting ice zero degrees, and that of boiling water, or more accurately, steam from water boiling under the normal atmospheric pressure, one hundred degrees, we shall have a scale for measuring differences of temperature. Thus, a body which is found to be in thermal equilibrium (i.e., neither grows cooler nor warmer when immersed in it) with a mixture of equal parts of boiling water and ice-water has a temperature fifty degrees higher than that of ice, or, in short, a temperature of 50°. Again, a body in thermal equilibrium, with a mixture of one fourth boiling water and three fourths ice-water, would have a temperature of 25°. The temperature of a body colder than ice would obviously have to be indicated by a negative number. It is important to observe that the numerical value of a temperature is merely the value of the difference of temperature between the substance and that of melting ice, measured in such units that 100 of them express the difference in temperature between ice and boiling water. Hence a temperature of 50° is in no sense twice as high as a temperature of 25°,

nor, from what appears in the definition, is there any numerical ratio between them.

Thermometers.—The method of determining differences of temperature indicated above is not a convenient one ; so, in practice, the variation in volume of some substance which is found to follow sufficiently closely the same rate as the variations of temperature is chosen. Of the various possible substances the only one which is generally used in chemical work is mercury, which, enclosed in a bulb provided with a tube of fine bore, constitutes the mercurial thermometer. Fig. 42 shows the form ordinarily used in the laboratory. Three processes are necessary to fit it for use. First, when sufficient mercury has been introduced into the bulb, the top of the tube is sealed after excluding the air by boiling the mercury; then the bulb and stem up to the top of the column are immersed in moist pounded ice until there is no further change and the position of the top of the column marked on the glass: this is the zero point. Second, the bulb and stem are immersed in steam issuing from boiling water, when the pressure of the atmosphere is 760 mm., and the position of the end of the column marked on the tube, giving the 100° point. Third, the stem is divided between these fixed points into one hundred parts of equal volume, and, if required, the division is carried on above and below the two points. In practice it is assumed that equal distances on the stem correspond to equal volumes, an approximation which is generally sufficient for carefully chosen tubes.

The thermometer so divided is universally used in chemistry, and is known as the centigrade thermometer. When there is any danger of confusing it with any other thermometric scale, it is the custom
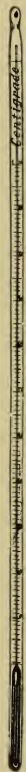
Fig. 42.

to write a capital C after the number expressing the reading; thus 30° C. is to be read, thirty degrees centigrade.

Calibration of Thermometer.—If, however, a more accurate knowledge of the thermometer is required, it will be necessary to calibrate the tube so as to determine the errors of such a number of points intermediate between 0° and 100°, that the errors for every portion may be safely inferred. The process is as follows. Having inverted the thermometer, tap it lightly against the lower end. Then either the thread will separate, or the mercury in the bulb will fill the tube, leaving a small space at the base of the bulb. If the latter is the case, the thermometer must be turned and the vacant space brought to occupy the region of the opening of the bulb—a condition which is always practicable. We thus secure finally a thread of mercury in the stem separated from the remainder by a vacant space. The length of this thread can be modified at will. Suppose, for example, we wish to make it n degrees longer. Erect the thermometer and allow the thread to run down to contact with the rest; then warm the thermometer n degrees, invert and tap again, and the thread will break at the same point as before, leaving thus an increased length of the desired amount. If, on the other hand, we wish a thread shorter by n degrees, we cool the bulb after the thread has been allowed to run down into contact with the remainder by this amount, and produce a separation again as before. The fracture of the thread is determined by the presence of a minute bubble of air which clings to the wall of the tube and does not move with the mercury. It is obvious that in this process the bulb should be warmed sufficiently to have the point of contact in the tube and not in the bulb.

Having thus secured a thread as nearly as may be of 50° in length, cause it to slide along the tube until one end is at 0° and the other, say, at 50°.6. Then shift the thread until the upper end is at 100°, the lower reading, say. 49°.7. Since the volume (V) of the mercury in the thread remains unchanged, this observation gives us

$$\text{Volume from 0 to 50} = \frac{50}{50.6} V,$$

$$\text{Volume from 50 to 100} = \frac{50}{50.3} V,$$

whence the ratio of the first volume to the second is $\frac{50.3}{50.6}$, and, since the temperature interval from the 0° point of the scale to the 100° point has

been determined by ice and boiling water, we have the temperature interval between the 0° point and the 50° point

$$\frac{50.3}{100.9} T,$$

if T is the former interval. Thus the true temperature corresponding to the thermometric reading 50° is $\frac{50.3}{100.9} T + k_0$, if k_0 is the correction to be added to the zero reading of the thermometer.

With a thread of nearly 25° in length it will be easy to determine by a precisely similar process the errors of the 25° and 75° points after having determined that of the 50° point, and so on for any number of aliquot subdivisions of the scale desired. In practice it will be found sufficient to determine these five points unless the errors are found to be considerable, in which case the thermometer should be rejected for all exact use.

Heat.—When equal quantities of two unlike substances at different temperatures are kept in contact until these temperatures are alike, it is found that the final temperature is in general very far from the average of the two. Since in this case we suppose that all the heat which has left the hotter body goes into the colder, we must conclude that it requires very different amounts of heat to raise like masses of different substances through the same range of temperature.

Exp. 1.—This important fact can be demonstrated qualitatively by placing a beaker of water over a Bunsen burner and noting the rate of the rise of temperature by means of a thermometer; then replace the water by an equal amount of some other liquid, say turpentine, and again note the rate of increase of temperature: it will be found to be much greater in the second case, more than twice as great if turpentine be used. As the source of heat is the same in the two cases, and all the other conditions are very nearly the same, we conclude that it requires more than twice the quantity of heat to raise a given quantity of water through a given range of temperature, than it does to raise a like quantity of turpentine through the same range.

Unit of Heat: Calorie.—In order to define a quantity of

heat we must therefore not only consider the change of temperature which it produces, but the magnitude and substance of the body in which the change is produced. The heat unit employed in chemistry is a quantity of heat which added to a gram of water at 0° C. would raise its temperature 1° C. This unit is called the calorie.

Specific Heat.—The specific heat of a substance is the ratio of the quantity of heat required to raise the temperature of one gram by 1° C. to the calorie.

Determination of Specific Heat.—We shall consider here only the method known as the method of mixture. Suppose we have a vessel (of thin metal by preference) containing M grams of water at a temperature t, into which we put m grams of the substance whose specific heat we wish to determine, at a higher temperature t'. The substance may be liquid or solid, but if the latter it should be in small pieces. After the temperature of the water and the substance has become the same, which can be hastened by stirring, read the temperature with a thermometer; call it t''. Then the rise of temperature of the water is $t'' - t$, and the fall of temperature in the substance is $t' - t''$; consequently the water has gained $M(t'' - t)$ calories, and, if s be the specific heat of the substance, the amount of heat lost by it is equal to $ms(t' - t'')$ calories. These two quantities must be equal if precautions have been taken against gain or loss from outside, hence

$$ s = \frac{M}{m} \frac{(t'' - t)}{(t' - t'')}. $$

Fusion.—When heat is added continuously to a solid its temperature rises continuously up to a certain point, when it commences to melt. If the mixture of the solid and liquid is constantly stirred, it is found that the temperature remains unchanged until it becomes entirely liquid. This fixed tem-

perature is called the melting point, and it is quite characteristic of a substance. The following table gives a number of melting-points. The higher temperatures are only approximate.

TABLE OF MELTING POINTS.

Mercury	−39°	Gold	1240°
Tin	228°	Copper	1330°
Lead	334°	Cast-iron	1200°
Zinc	423°	Wrought-iron	1600°
Silver	1000°	Platinum	2000°

Vaporization.—If heat is added continuously to the bottom of a liquid, the temperature rises until bubbles of vapor form at the lower surface and rise through the body of the liquid. This phenomenon is called boiling, and it is found that the temperature remains unchanged until all the liquid has been converted into vapor. The temperature of boiling is always the same for the same liquid, provided that the pressure is the same; but it varies greatly with the pressure. By the *boiling point* is meant the temperature of a boiling liquid under the standard atmospheric pressure, namely, 760 mm., mercury column. The following table contains some of the more important boiling points. The very low and very high boiling points are only approximate.

TABLE OF BOILING POINTS.

Hydrogen	−215°	Water	100°
Oxygen	−181°	Mercury	350°
Carbon dioxide	− 78°	Sulphur	448°
Ammonia	− 34°	Zinc	1040°
Sulphur dioxide	− 10°	Silver	Oxyhydrogen flame.
Ether	35°	Platinum and other difficult-	
Alcohol	78°	ly volatile metals	In voltaic arc.

Latent Heat of Fusion.—To convert a given quantity of a solid into a liquid at the same temperature requires the addi-

tion of a large quantity of heat. Since the addition of the heat is unaccompanied by rise of temperature the heat thus expended is called *latent heat.*

Exp. 2.—Mix 150 grams of water at 100° with 100 grams of ice at 0°. The ice will be melted and the temperature of the mixture will be about 28°.3 C. (exactly if the experiment be very accurate). In this case the water has lost 10,755 calories, and the water of the melted ice has gained 2830 calories. The difference is 7925 calories, which has been employed in converting the 100 grams of ice at 0° into water at 0°; hence it requires 79.25 calories to convert a gram of ice into a gram of water at the same temperature. This number is called the latent heat of fusion of ice.

Bunsen's Ice Calorimeter—If a body at a temperature, say, of 100° C. is placed in a cavity in a block of ice at 0° C. it will finally attain the same temperature as the ice, after having melted a certain number of grams. The number of grams of water from the melting multiplied by 79.25 will give

the number of calories lost by the body, which, divided by the product of the mass of the body by the product of its fall in temperature, gives the numerical value of the specific heat. This principle is the basis of Bunsen's calorimeter, an apparatus which has proved of great value to chemistry, because it admits of accurate determination of the specific heat of a very small quantity of a substance. It consists of a glass vessel, *A* (Fig. 43), having sealed into it a closed tube *B*, and a fine graduated tube *C*. The tube *C*, together with a portion of the vessel *A*, is partially filled with mercury, the remaining portion of *A* which surrounds *B* being filled with water carefully freed from air.
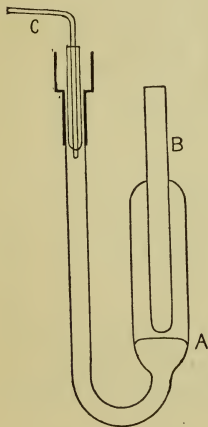
FIG. 43.

Then a current of alcohol at a temperature below zero is passed through the tube B until all of the water in A is frozen. Since ice is nearly one tenth more bulky than the water from which it is derived, a portion of the mercury will escape from C during this process. Next, the whole apparatus being buried in moist snow, the temperature throughout finally becomes zero, and the end of the thread of mercury assumes a fixed position in C. Let this position in the graduated tube be designated by a. Now, after having removed the cold alcohol, drop a gram of water at 100° into the tube B, a certain portion of the ice will be melted, and the end of the thread of mercury will be retracted, reaching finally, after the water has cooled to 0°, a position on the scale b. Thus a change of $b - a$ divisions on the scale corresponds to an addition of 100 calories to the calorimeter. If now a gram of the substance to be tested at a temperature of 100° is dropped into the tube B, more ice will be melted and the thread will be farther retracted to the point c; consequently the ratio of the heat lost by the substance to that lost by the gram of water is $c - b : b - a$; but this is obviously the specific heat of the substance, as appears from the definition. Since the temperature of 100° can be accurately secured by keeping the substance in a vessel immersed in steam from boiling water sufficiently long it is obvious that no thermometer is required in the experiment.

Pressure and Volume of Gases.

Barometer.—The pressure of the atmosphere can always be determined by the barometer. This, in the form used in the laboratory, consists of a glass tube closed at the upper end and bent in U form near the lower end, as in Fig. 44. The distance from the bend to the closed end must be considerably greater

than 76 cm.   Into the tube, when held in a reversed position
from that in the figure, are introduced suc-
cessive small quantities of mercury, which are
boiled over a lamp so as to expel all the air
clinging to the glass and to the surface of the
mercury.   When this process has been car-
ried on until the tube is full to the bend, it
is erected and the mercury falls a certain
distance in the long arm, leaving a vacuum
above.   The difference of level in the free
surfaces of the mercury is determined from
millimeter graduations on both arms of the
tube, and is found
to be at the sea-
level about 760 mm.
Since the atmos-
pheric pressure is
cut off from the
upper end of the
tube, it is obvious
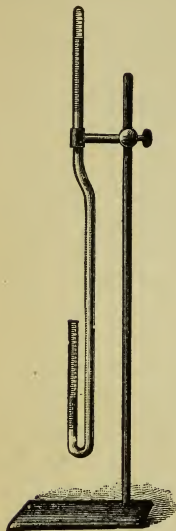
FIG. 44.

that the pressure of the air on the
free surface of the mercury in the
short tube is equal to the pressure
due to the weight of a layer of mer-
cury whose depth is equal to the
difference of level in the two arms.
The difference 760 mm. is taken as
the measure of the standard at-
mospheric pressure.   This arbitrary
unit of pressure is designated by the
term *atmo*.

FIG. 45.

Measurement of Gases.—By means
of a barometer and a graduated tube closed at one end, it
is easy to measure the volume and pressure of a quantity of

gas.　Suppose the tube to be graduated to cubic centimeters from the closed end.　If it be filled with mercury, inverted with its open end under the surface of a vessel of mercury, and a sufficient quantity of gas be then introduced into the tube, it will assume the appearance of Fig. 45.　The volume of the gas can be read at once from the tube, while its pressure is equal to that of the external atmosphere diminished by that due to a column of mercury of height x.　The pressure is then, if h is the observed height of the barometer, $\dfrac{h-x}{760} \times$ atmo., where all the lengths are measured in milli-meters.　A thermometer suspended in contact with the tube will give the temperature of the gas.

Laws of Gases.

The law connecting pressure and volume of a gas at constant temperature, known as Boyle's law, has already been given.　It may be formulated thus:

$$pv_t = k \ [t \text{ constant}],$$

where p equals pressure, v_t the volume at temperature t, and k a constant.

The law connecting volume and temperature at constant pressure is equally simple.　It has been found that all gases expand $\frac{1}{273}$ of their volume at $0°$ C., for each increase of one degree in temperature, provided that the pressure remains unchanged.　This law, discovered by Charles but commonly known as that of Gay-Lussac, may be formulated thus:

$$v_t = v_0(1 + \tfrac{1}{273}t) \ [p \text{ constant}],$$

where v_t equals the volume of the gas at the temperature t, v_0 the volume at $0°$ C., t the temperature on the centigrade scale, and p the pressure.

3

These two equations can be combined so as to yield a single equation applicable to all cases; for let P represent the standard atmospheric pressure and V_0 the volume of the gas under this pressure and at a temperature of zero, then the first equation gives

$$pv_0 = P V_0 = k,$$

and the second gives a value for v_0, which, substituted here, yields

$$P V_0 = p \frac{v_t}{1 + .00367t},$$

where the value of the fraction $\frac{1}{273}$ is expressed by the decimal .00367. Thus, if we observe the volume v_t of a gas under a pressure p and at a temperature t, we can find from this formula what its volume should be at a temperature $0°$ and at atmospheric pressure even if the substance in question cannot exist as a gaseous body at that pressure and temperature. We may make a convenient modification of this formula to adapt it to practice. Since gaseous pressures are in direct ratio to the heights of the columns of mercury which they will sustain, and the normal atmospheric pressure is assumed to be equal to that of a column of mercury 760 mm. in height, we may write

$$V_0 = \frac{h}{760_{mm}} \frac{v_t}{1 + .00367t},$$

where h is to be measured in millimeters.

Kinetic Theory of Gases.

Kinetic Theory.—A gas has been defined as an aeriform body which obeys Boyle's Law, i.e., as one in which the pressure at constant temperature is inversely as the volume. Hence if the pressure be diminished without limit the volume would increase without limit, or, in other words, the mole-

cules would separate indefinitely from each other. The most obvious conclusion is that the molecules repel each other; but Daniel Bernoulli pointed out before the middle of the last century that it is impossible to assign any law of repulsion which would make the pressure independent of the shape and size of the containing vessel—in short, which would make the pressure follow the well-known law. He showed, also, that if all the particles be regarded as in motion, the pressure might be explained by the collision of the molecules against the sides of the vessel. This general explanation has received a wide development during the last forty years, under the name of the Kinetic Theory of Gases.

Explanation of Gaseous Pressure.—The fundamental suppositions of the kinetic theory are, first, that every body of gas which can be experimented upon contains a practically infinite number of molecules; second, that all the molecules are in continuous motion with a high velocity; third, that the dimensions of the molecules are very small compared to their average distance apart; and, fourth, that the time during which any one molecule is near enough to any other to act upon it is very brief compared to the time that it is too remote from all others to affect them.

With these suppositions it is easy to find an expression for the pressure of a gas in terms of its density and the average velocity of its molecules.

Let Fig. 46 represent a rectangular box having the edges a, b, c, filled with gas. Let

p = pressure of the gas.

N = number of molecules in one cc.,

m = mass of each molecule,

$\rho = Nm$ = density of gas,

V = average velocity of motion of molecules.
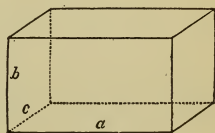
FIG. 46.

If a molecule strikes normally against a side of the vessel,

say the side bc, it will, on the average, bound off with the same velocity with which it struck; the motion is thus changed from mV to $-mV$, a total change of $2mV$, by the reaction of the wall. Since force is measured by the rate at which it changes motion, the average force exerted by the wall upon the molecule is $\dfrac{2mV}{\tau}$, if τ is the duration of the whole action. Now by the second supposition the number of molecules, and hence the number of molecular impacts per second, is indefinitely great; therefore the force exerted by the wall is constant, and equal to $\dfrac{2mV}{\tau}$ multiplied by the number of impacts in the time τ. To find the whole constant force upon bc, then, we have only to find the number of molecules which strike against it during the time τ.

It is obvious that we shall not be very far from the truth in calculating the number of impacts if we make the simple suppositions, first, that all the molecules have the constant velocity of the average, and, second, that a third of the molecules are moving parallel to each of the three edges a, b, and c.

The first supposition gives the number of times which any one molecule of those which move parallel to a strikes the side bc in a second as $\dfrac{V}{2a}$, or during the time τ as $\dfrac{V}{2a}\tau$. This, with the second supposition, since the whole number of molecules in the box is $Nabc$, gives

$$\frac{1}{3}Nabc\frac{V}{2a}\tau = \frac{1}{6}NbcV\tau$$

as the number of molecular impacts on bc during the time τ. We thus have the total constant force exerted by the face bc,

$$F = \frac{1}{3}NmbcV^2.$$

But pressure is defined as force divided by area upon which it is exerted; hence

$$p = \frac{1}{3}Nm\,V^2 = \frac{1}{3}\rho\,V^2.$$

But this is obviously the law of Boyle.

Calculation of Molecular Velocities.—From the last equation we have

$$V = \sqrt{\frac{3p}{\rho}}.$$

In order to reduce this we must express p in the same units as are chosen for V and ρ, namely, in centimeters, grams, and seconds. As a special example, we will find the molecular velocity for air at 0°C. and 76 cm. pressure, measured in mercury column.

The pressure at the base of a mercury column 76 cm. in height is 76 × 13.6 grams weight per square centimeter. But if a gram be allowed to fall freely it is found that during the first second it will have acquired a velocity of 980 cm. per second, that is, a gram weight is 980 times the unit of force defined in terms of the gram, centimeter, and second, or 980 dynes. Again, experiment, such as described on p. 10, shows that the density of air at 0° and atmospheric pressure is $\frac{1}{773}$, hence, substituting these values,

$$V = \sqrt{3 \cdot 76 \cdot 13.6 \cdot 980 \cdot 773} = 48500 \text{ cm.}$$

Again, since the molecular velocity for a gas at 0° varies inversely as the square root of the density, we may find the velocity for any other gas by multiplying this number by the square root of the ratio of the density of air to that of the gas in question; e.g., air is 14.44 times as dense as hydrogen, hence the mean value for the velocity of a hydrogen molecule at a temperature of 0° is 48500 cm. × $\sqrt{14.44} = 184300$ centimeters per second, approximately 1 mile per second.

In the above calculation the supposition which is most questionable, and which would give rise to the greatest errors in the results, is the first, namely, that the molecular velocities are all equal. For even if this equality of velocities existed for a moment it would be immediately destroyed by mutual molecular collisions, and inequality follow. Taking into account, however, this fact of constantly varying velocities, Maxwell has found that the average velocities are $\frac{12}{13}$ of these, calculated according to the simple methods above. Thus corrected, the mean molecular velocities for a number of substances at 0° is given below:

Hydrogen, ... 1698 meters.	Carbon dioxide, . . 361 meters.
Water vapor, . . . 566 "	Chlorine, ... 286 "
Nitrogen, ... 453 "	Bromine, ... 190 "
Air, ... 447 "	Mercury, ... 169 "
Oxygen, ... 425 "	Iodine, ... 151 "

Law of Avogadro.—The most important result of Maxwell's investigations into the laws of molecular motion in a gas was the proof that in any two gases at the same temperature the products of the molecular mass into the square of the average molecular velocity are equal. Hence, if we have two gases, 1 and 2 at the same temperature,

$$m_1 V_1^2 = m_2 V_2^2.$$

Also, if the pressures be the same, $N_1 m_1 V_1^2 = N_2 m_2 V_2^2$, each of these two equal quantities being three times the pressure. Dividing the second quantities by the first, we have

$$N_1 = N_2;$$

that is, *In equal volumes of any two gases at the same pressure and temperature there are an equal number of molecules.* This law, of the highest value in chemistry, is known as the Law of Avogadro; it enables us to determine the relative masses of the molecules of all substances which can be experimented upon in the gaseous condition.

Diffusion.—Suppose the box (Fig. 46, p. 35) to have a small opening of area s in the end bc; then, as appears from the reasoning on p. 36, the number of molecules which would reach the aperture per second and escape from the box would be $\frac{1}{6} N s V$. For all gases, however, pressure and temperature being the same, N is the same; hence the rate at which the gas would escape would be proportional to V, or inversely proportional to the square root of the density, since V for different gases varies in this ratio. This conclusion is found to be in accordance with experience.

Again, suppose the box divided into two sections by a porous partition, say of plaster of Paris or of unglazed earthenware, which may be regarded as a wall with innumerable small openings in it. If the sections be filled with gases at like pressures and temperatures, but of unlike densities, and consequently of unlike molecular velocities, more of the lighter molecules will penetrate the porous partition in a given time than of the denser, hence the pressure will at first increase on the side of the denser gas, and decrease on the other. Finally, however, the mixtures will become alike on the two sides of the diaphragm.
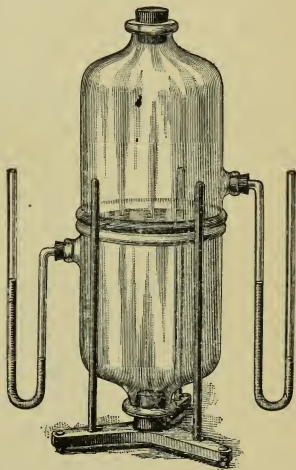
FIG. 47.

Exp. 3. Diffusion of hydrogen.—Fig. 47 represents two bell-jars, the upper one of which is closed at its base by a plate of plaster of Paris, each having a manometer tube attached. The bases of the jars are ground true, and greased so as to fit together gas tight.

To make the experiment, remove the manometer tubes and place the upper jar on a glass plate, and fill it with hydrogen by passing a rapid current of the gas into the jar through the lower tubulure. Next,

place the jars in position as shown in the figure, and quickly adjust both manometer tubes at the same instant.

The manometers will show a marked decrease of pressure in the upper jar and an equal increase in the lower. After some time this difference of pressure will attain a maximum, and then slowly disappear.

We can draw a conclusion of great interest to the science of chemistry from an experiment of this kind. Suppose in the box, arranged as last described, one of its divisions only be filled with a gas, e.g., hydrogen, the other division being left empty; then, if hydrogen consists of molecules of different masses, since the lighter ones must have a higher average velocity in accordance with Maxwell's law, we should be able to sift out the lighter molecules and thus secure a hydrogen of less density than that with which we started. As such separation is found to be impossible, we conclude that all the molecules of a gas are alike.

Size and Number of Molecules.—The average distance that a gaseous molecule will move before coming into a collision with another is called the mean free path. This depends evidently upon the average space occupied by each molecule, and the cross-section of the molecule; for if either the density of the gas or cross-section be diminished the relative portion of the space occupied by matter will be reduced, and the chance of a molecule going a longer distance before meeting another will be increased. The law connecting these three quantities has been deduced from the kinetic theory of gases, so that if any two of them are known from observation the third can be calculated. But the mean free path can be derived from observations on the viscosity of gases with considerable precision. On the other hand, although we have no means of finding exactly the cross-section of the molecules, still the great incompressibility of liquids suggests that the molecules are probably not far removed from contact; hence if the volume of a gas when condensed to the liquid form is known, we may estimate the sum of the cross-sections of all the molecules contained in

a unit volume of the gas. These two data yield a value for the number of molecules in unit volume of the gas, and therefore the approximate size also. This process applied to the gases carbon dioxide, hydrogen, and air give diameters 0.18, 0.14, and 0.30 millionths of a millimeter, respectively. These values, all of the same order of magnitude, do not differ greatly from other estimates made by entirely independent methods, and are thus entitled to considerable confidence. It is certainly hardly possible that they are either ten times too great or ten times too small.

The same process yields the number of molecules in a cubic centimeter of air, or, in accordance with Avogadro's law, in a cubic centimeter of every gas. It is, for atmospheric pressure and 0° C.,

$$21(10^{18}),$$

or, 21 millions of millions of millions. Since we cannot observe a gas under a pressure many hundreds of times less than the atmospheric pressure, it is obvious that we are always justified in assuming that every body of gas observed contains practically an infinite number of molecules.

Determination of Gas Densities.

The important principle stated on p. 38, and known as Avogadro's law, enables us to determine the ratio of the mass of any gaseous molecule to that of a molecule of hydrogen if we know the ratio of the density of the gas to that of hydrogen at the same temperature and pressure. The determination of this density ratio, commonly called the *gas density* or *vapor density*, becomes thus a process of fundamental importance in chemistry. There are many ways of doing this, each of which possesses advantages of its own; but the method devised by Victor Meyer for determining the gas densities of substances which are ordinarily in the solid or liquid state, but which may

be made to assume the gaseous condition at a temperature below the point at which glass softens, and at a moderate pressure, is of extraordinary simplicity.

The apparatus employed is shown in Fig. 48, *a*. It consists of a glass cylindrical vessel *B*, of about 100 cc. contents and a length of 200 mm., to which is sealed a tube of about 600 mm. in length and 6 mm. in diameter, ending above in an enlarged mouth stopped by a rubber stopper. A little below the upper end is a small branch tube *A*, the end of which, bent upwards, is below the surface of a vessel of water *D*. If a temperature not exceeding 310°, the boiling-point of diphenylamin, is sufficient, the tube *B* is surrounded by a larger glass tube ending in a bulb *C*, which contains the liquid for heating the tube *B*. This liquid may be water (to 100°), aniline (to 183°), amylbenzoate (to 260°), or diphenylamin (to 310°). For still higher temperatures the vessel *B* is introduced into a piece of closed iron gaspipe *M*, which is surrounded by melted lead contained in the larger pipe *N*, Fig. 48, *b*.
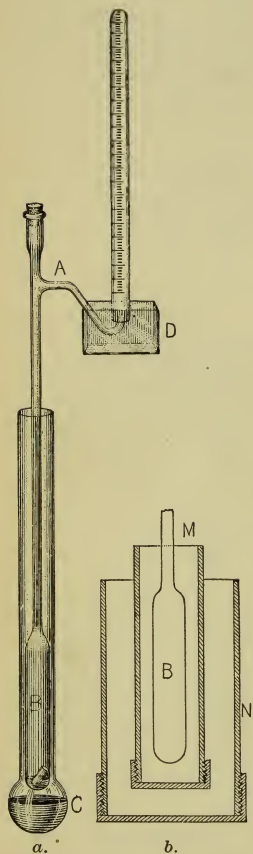
To determine the gas density of a substance a quantity is weighed out, which, when gasified, will not more than half fill the vessel *B*. This is enclosed in a little glass flask sufficiently small to drop through the tube into *B*. After the apparatus has attained a constant

FIG. 48.

temperature so that there is no further escape of air through the tube A, the stopper is removed, the substance dropped into B, where there is a cushion of asbestus to protect the glass, and the stopper immediately replaced. As this is pushed in one or two bubbles of air will escape from A, after which the inverted graduated tube, quite full of water, is to be placed over the end of A. The substance will evaporate in a few seconds, and its gas will drive out its own bulk of air which will collect in the graduated tube. After the flow of air has ceased, the graduated tube is lowered in the water until the level of the surface of the water inside and outside is the same, and the volume of the air is read from the graduation, together with its temperature, by means of a thermometer. This, with a reading of the height of the barometer, completes the observations.

The reduction of the observation is as follows. It is obvious that the mass of the gas formed from the substance is the same as the mass of the substance, and is consequently known. Let this mass be m. The mass of the air displaced may be represented by m', and its observed volume by v. Since the density of air is 14.44 times as great as that of hydrogen, we have the gas density of the substance, as defined above, equal to $D = \dfrac{m}{m'} 14.44$.

It only remains to find the value of m'. As appears on p. 10, the mass of a cubic centimeter of air at a temperature $0°$ and a barometric pressure of 760 mm. is $\frac{1}{773}$ of a gram; but by the law of Boyle and Charles, p. 34, we can find the volume reduced to this standard temperature and pressure, when the volume, temperature, and pressure are known. Thus,

$$V_0 = \frac{h}{760 \text{ mm.}} \frac{v_t}{(1 + .00367t)},$$

and

$$m' = \frac{V_0}{773} \text{ grams.}$$

In these formulas V_0 is the reduced volume, v_t the observed volume, h the barometric reading at the time of the experiment, and t the temperature.

This process would be complete if the displaced air were collected over mercury, but as it is more convenient to collect over water, a connection is required for the vapor of water, which is mixed with the air in the graduated tube. As the air has not only passed through the water in small bubbles, but has stood in contact with it for some time, we may safely assume that at the time of reading the volume the pressure of the water vapor is as great as possible under the existing condition of temperature, and can be found from the table of maximum pressures of water vapor given on page 113, corresponding to the observed temperature. Let this pressure be denoted by w. It is obvious that the whole pressure in the graduated tube, measured by h, is the sum of the pressures of the air and of the water vapor; hence the pressure of the air is measured by $h - w$, which is to be substituted in the equation above. Making this substitution, we have

$$V_0 = \frac{h - w}{760} \frac{v_t}{1 + .00367t},$$

$$m' = \frac{V_0}{773};$$

and finally,

$$D = 14.44 \frac{m}{m'} = \frac{14.44m \cdot 760 \cdot 773(1 + .00367t)}{(h - w)v_t}.$$

Carrying out the multiplications of the constants, we may write

$$D = 8484000 \frac{m(1 + .00367t)}{(h - w)v_t}.$$

The results of some of Meyer's determinations, and a comparison with the values calculated from theory, according to methods given farther on, may be given here.

Chloroform [heated in steam].

$m = 0.1008 \qquad t = 16°.5 \qquad h = 707.5 \qquad v = 22 \quad$ cc.

D 59.4 observed, 59.7 calculated.

Carbon Disulphide [in steam].

$m = 0.0495 \qquad t = 16°.5 \qquad h = 717.8 \qquad v = 16.4$ cc.

D 38.6 observed, 38.0 calculated.

Iodine [in amyl benzoate].

$m = 0.1157 \qquad t = 16°.1 \qquad h = 722.3 \qquad v = 11.6$ cc.

D 126.4 observed, 127.0 calculated.

Mercury [heated in lead bath].

$m = 0.0905 \qquad t = 16°.0 \qquad h = 715.8 \qquad v = 11.5$ cc.

D 100.7 observed, 100.0 calculated.

The student should make several determinations of gas density, or if this is not practicable, the instructor should make them and let the class make the required calculations.

CHEMISTRY.

Elements, Atoms, Classification.

Elements.—A substance which cannot be resolved into two or more different substances is called an element or simple body. Gold, silver, iron, copper, lead, tin, sulphur, oxygen, nitrogen, and iodine are familiar examples of elementary substances.

Chemical compounds are composed of two or more elements held together by their mutual chemical attraction. The means at our command for the decomposition of compounds are heat, electricity, light, and chemical action. Our experimental work will make us acquainted with the application of these agents not only in isolating elements, but also in effecting chemical changes.

We have already learned from the kinetic theory of gases that a substance in the gaseous state is composed of very small particles, molecules, having definite mass. Most molecules are composed of parts which cannot be divided into smaller parts. These indivisible particles are called **Atoms**. Since atoms rarely exist in the free state, and only at very high temperatures, the following definition may be given. *An atom is the smallest particle of matter existing in combination.*

The evidence of the existence of atoms is chemical, and we can therefore best study the atomic theory after having become familiar with a large number of chemical facts. Since we shall use, in beginning the study of chemistry, the terms

atom and atomic weight, we shall need some idea of their meaning. The atoms of an element are alike in all respects; the atoms of different elements, that is, different kinds of atoms, differ in mass, and more or less in other properties. The distinguishing characteristics of a mass of matter are determined by the properties of the individual atoms which compose it.

An atomic weight is a number expressing the ratio of the mass of the smallest particle of an element entering into combination, to the mass of an atom of hydrogen or half the molecule of hydrogen.

It is obvious from the definition that an atomic weight, or a multiple thereof, represents the relative weight of an element taking part in chemical changes.

Symbols.—Chemists represent the elements by symbols which are the initial letters of their names, or the initial letter and one other. Some of the symbols are from the Latin or other names. A symbol of an element stands for an atom, and also for an atomic weight.

Formulas.—The number of atoms in a molecule of an element is indicated by a number placed below and to the right of the symbol: thus, H_2 indicates that the molecule of hydrogen contains two atoms. A compound is represented by the symbols of its constituents: thus, hydrogen chloride, a compound of hydrogen and chlorine, has the symbol HCl. This represents one atom and 1 weight of hydrogen, one atom and 35.5 weights of chlorine. Likewise, the composition of water is best shown by the symbol H_2O, which represents two atoms and 2 weights of hydrogen, and one atom and 16 weights of oxygen.

The calculation of the percentage composition of a compound whose formula is given is a simple arithmetical process which requires no explanation.

The following is an alphabetical list of the 68 elements recognized up to the year 1888, together with their symbols and atomic weights; the names of the rarer elements are in italics.

Aluminum,	.	.	**Al** 27	*Molybdenum,*	. .	**Mo** 96
Antimony,	.	.	**Sb** 120	Nickel,	. . .	**Ni** 58
Arsenic,	.	.	**As** 75	*Niobium,*	. . .	**Nb** 94
Barium,	.	.	**Ba** 137	Nitrogen,	. . .	**N** 14
Beryllium,	.	.	**Be** 9	*Osmium,*	. . .	**Os** 192
Bismuth,	.	.	**Bi** 208	Oxygen,	. . .	**O** 16
Boron,	.	.	**B** 11	*Palladium*	.	**Pd** 106
Bromine,	.	.	**Br** 80	Phosphorus,	. .	**P** 31
Cadmium,	.	.	**Cd** 112	Platinum	. .	**Pt** 195
Cæsium,	.	.	**Cs** 133	Potassium (kalium),	.	**K** 39.1
Calcium,	.	.	**Ca** 40	*Rhodium,*	. .	**Rh** 104
Carbon,	.	.	**C** 12	*Rubidium,*	.	**Rb** 85.5
Cerium,	.	.	**Ce** 141	*Ruthenium,*	.	**Ru** 103
Chlorine,	.	.	**Cl** 35 45	*Samarium,*	. .	**Sm** 150
Chromium,	.	.	**Cr** 52.5	*Scandium,*	. .	**Sc** 44
Cobalt,	.	.	**Co** 59	*Selenium,*	. .	**Se** 79
Copper (cuprum),	.		**Cu** 63.3	Silicon,	. . .	**Si** 28
Didymium,	.	.	**D** 145	Silver (argentum),	.	**Ag** 107.9
Erbium,	.	.	**E** 166	Sodium (natrium),	.	**Na** 23
Fluorine,	.	.	**F** 19	Strontium,	. .	**Sr** 87.5
Gallium,	.	.	**Ga** 70	Sulphur,	. .	**S** 32
Germanium,	.	.	**Ge** 72	*Tantalum,*	. .	**Ta** 183
Gold (aurum),	.	.	**Au** 196.7	*Tellurium,*	. .	**Te** 125
Hydrogen,	.	.	**H** 1	*Thallium,*	. .	**Tl** 204
Indium,	.	.	**In** 113.7	*Thorium,*	. .	**Th** 232
Iodine,	.	.	**I** 127	Tin (stannum),	.	**Sn** 118
Iridium,	.	.	**Ir** 193	*Titanium,*	. .	**Ti** 48
Iron (ferrum),	.	.	**Fe** 56	*Tungsten* (wolfram),		**W** 184
Lanthanum,	.	.	**La** 139	*Uranium,*	. .	**Ur** 239
Lead (plumbum),	.		**Pb** 207	*Vanadium,*	. .	**V** 51.3
Lithium,	.	.	**Li** 7	*Ytterbium,*	. .	**Yb** 173
Magnesium,	.	.	**Mg** 24.4	*Yttrium,*	. .	**Y** 89
Manganese,	.	.	**Mn** 55	Zinc,	. . .	**Zn** 65.4
Mercury (hydrargyrum),			**Hg** 200	*Zirconium,*	. .	**Zr** 90.7

Classification of the Elements.—The classification of the elements adopted in this book is that known as the *Periodic System of the Elements.* In this system the elements are arranged according to increasing atomic weights, and in groups whose members are more or less closely related in properties. The following is Mendelejeff's table* with a few minor changes:

GROUPS.			PERIODS.					
			I.	II.	III.	IV.	V.	VI.
R_2O	I.	——	Li 7	K 39	Rb 85.5	Cs 133	——	——
RO	II.	——	Be 9	Ca 40	Sr 87.5	Ba 137	——	——
R_2O_3	III.	——	B 11	Sc 44	Y 89	La 139	Yb 173	——
RO_2	IV.	(H_4C)	C 12	Ti 48	Zr 90.7	Ce 141	——	Th 232
R_2O_5	V.	(H_3N)	N 14	V 51	Nb 94	Di 145 Sm 150	Ta 183	——
RO_3	VI.	(H_2O)	O 16	Cr 52.5	Mo 96	——	W 184	U 239
R_2O_7	VII.	(HF)	F 19	Mn 55	——	——	——	——
RO				Fe 56	Ru 103	——	Os 192	——
to	VIII.	——	——	Co 59	Rh 104	——	Ir 193	——
RO_4				Ni 58	Pd 106	——	Pt 195	——
R_2O	I.	H 1	Na 23	Cu 63.3	Ag 107.9	——	Au 197	——
RO	II.	——	Mg 24.4	Zn 65.4	Cd 112	——	Hg 200	——
R_2O_3	III.	——	Al 27	Ga 70	In 113.7	Er 166	Tl 204	——
RO_2	IV.	(H_4R)	Si 28	Ge 72	Sn 118	——	Pb 207	——
R_2O_5	V.	(H_3R)	P 31	As 75	Sb 120	——	Bi 208	——
RO_3	VI.	(H_2R)	S 32	Se 79	Te 125	——	——	——
R_2O_7	VII.	(HR)	Cl 35.5	Br 80	I 127	——	——	——

There are several other forms of tables of the periodic classification, but all based on the same principles. The order of treatment adopted in this book may be briefly stated. First, hydrogen is described; then the seventh group is con-

sidered, together with the compounds its members form with each other and with hydrogen. The first, sixth, second, fifth, third, fourth, and eighth groups are taken up in the order named. As a rule, only those compounds are described which an element forms with elements previously studied.

The student will find it necessary to look up the properties of many substances before studying them systematically, and in order to find them he should use the index. If the beginner will in addition frequently refer to larger works, such as Roscoe and Schorlemmer's Treatise on Chemistry, and Watt's Dictionary of Chemistry, for a description of substances in which he is interested, he will early form the invaluable habit of using the literature of chemistry.

Hydrogen, H.

Atomic Weight 1. *Molecule* H_2.

Hydrogen is a constituent of water, of animal and vegetable matter, and enters into the composition of a very large number of artificial compounds. Free hydrogen has been detected in volcanic gases, but is not found in ordinary atmospheric air.

Hydrogen is a colorless, odorless gas, and is the lightest known form of matter, being 14.44 times lighter than air. One liter of hydrogen at 0° and 760 mm. pressure weighs 0.0896 gram. The density of hydrogen in the alloy it forms with the metal palladium is 0.62; lithium, the lightest of metals, having a density of 0.59. Hydrogen was formerly regarded as a permanent gas, because it was found to remain in the gaseous state when subjected to enormous pressure. It was first liquefied by Cailletet in December, 1877, and independently by Pictet in the following month. Both experimenters exposed the gas to very low temperatures and great pressures. Pictet's result was attained at − 140° and a pressure of 650 atmospheres. When the apparatus containing the liquefied gas was opened steel-gray particles shot out

which rattled on the floor like a metal, the liquid hydrogen having been frozen by its own evaporation. The boiling-point of liquid hydrogen is about − 215°.

Exp. 4.—Weigh accurately a thin glass tube of size shown in Fig. 49. Cut the coating from the end of a piece of sodium and push the tube

FIG. 49.

into the metal until nearly filled. Cut away the sodium from about the tube, then push with a match-stick the sodium in the tube down about 2 mm. from the open end. Wipe the tube carefully, weigh quickly, and then place in rock-oil in which sodium has been kept. The metal cannot be kept in the air.
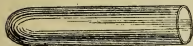
but the small surface exposed at the end of the tube will change very little during the weighing.

Seize the tube with forceps and place it under the graduated tube *A*, Fig. 50, which has been previously filled with water. Hydrogen gas will be set free, and in a short time the sodium will be dissolved in the water. Sink *A* in the water in *B*, and take the temperature of the water, which will be that of the gas. Next raise the graduated tube until the water in it stands at the same level as in the cylinder, thus making the pressure of the gas the same as that of the air. Note the number of cubic centimeters of gas and the height of the barometer. Calculate * the weight of the hydrogen obtained, and divide the weight of sodium taken by it. The result will show that 23 weights of sodium are required to set free one weight of hydrogen from water.
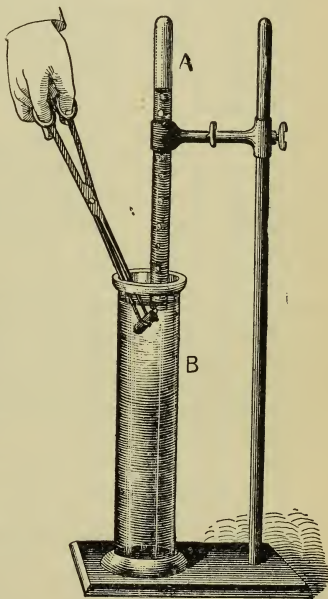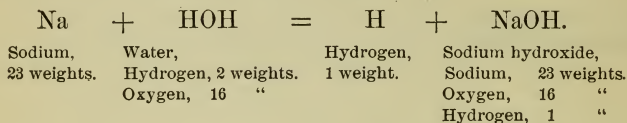

FIG. 50.

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* One experiment was as follows :

Tube and sodium............	0.5214 gram.
Tube......................	0.3335 "
Sodium............	0.1879 gram.

The atomic weight of sodium (see table of atomic weights) is 23; hence the conclusion from the foregoing experiment that each atom of sodium sets free one atom of hydrogen in the chemical change which occurs when sodium decomposes water. The reaction may be formulated as follows:

$$Na \quad + \quad HOH \quad = \quad H \quad + \quad NaOH.$$

Sodium,	Water,	Hydrogen,	Sodium hydroxide,
23 weights.	Hydrogen, 2 weights.	1 weight.	Sodium, 23 weights.
	Oxygen, 16 "		Oxygen, 16 "
			Hydrogen, 1 "

The equation represents not only that hydrogen is separated from water, but also that sodium replaces part of the hydrogen in water with formation of sodium hydroxide, a compound described later.

Equations which represent known chemical changes are based on the results of experiments in which the weights of part or all of the elements reacting have been determined. Chemists, however, often express a hypothesis regarding a reaction by an equation.

Exp. 5.—Remove the tube C, Fig. 51, and the rod supporting it, from the graduated tube B, and put into C about 0.3 gram of pure zinc, accurately weighed, and best in the form of a thin strip. Replace C in B, and while holding the cylinder D horizontally lay B in it. Next, set the apparatus upright, pour some water into D, and fill B with water by sucking at A.

Hydrogen .... 99.5 cc. at 19°.
Barometer .... 763 mm.
Pressure of aqueous vapor at 19°............ 16.3 "

Pressure of hydrogen .... 746.7 mm.

$$\frac{746.7 \times 99.5}{760 \times 1 + (.00367 \times 19)} = 91.4 \text{ cc. the volume at } 0° \text{ and } 760$$
mm. pressure.

91.4×0.0000896 (the weight of 1 cc. of hydrogen) $= 0.00819$ gram, the weight of the hydrogen obtained.

$0.1879 \div 0.00819 = 22.94.$

Hence 1 weight of hydrogen was set free by 22.94 weights of sodium. In another experiment 22.90 was the result.

Place in *A* a drop of solution of platinum chloride and some concentrated hydrochloric acid. Allow the acid to run into *B*, taking care that no air enters. After the liquid in *B* has fallen below *C*, more acid may be added to *B*. When the zinc has disappeared fill *A* with water and pass the water into *B*, and repeat the washing three or four times in order to remove most of the acid from the tube. Fill *D* with water, and raise *A* until *C* and the rod fall out. Finally, observe the temperature of the water, the volume of the gas, and the height of the barometer, and from these data calculate the relation between the weight of the zinc taken and that of the hydrogen obtained. Repeat the experiment until the results agree closely, and are very nearly 1 of hydrogen to 32.5 of zinc.

The apparatus described in the above experiment is a modification of that devised by Keiser,* whose form of apparatus is also good.

The atomic weight of zinc is 65, and the foregoing experiment shows that 65 weights of zinc set free 2 weights of hydrogen ; that is, 1 atom of zinc replaces 2 atoms of hydrogen. Hydrochloric acid has the formula HCl, Cl standing for the element chlorine. The zinc unites with the chlorine to form the compound zinc chloride, $ZnCl_2$, which is dissolved in the water. What is the equation representing the reaction between zinc and hydrochloric acid ?

Hydrogen is also made by adding sulphuric acid, H_2SO_4, diluted with water, to zinc, and in other ways.
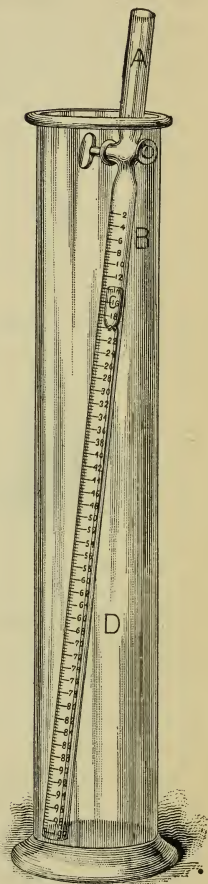

FIG. 51.

Exp. **6**.—Place in the bottle *A*, Fig. 52, about 100 grams of granulated zinc, pour through the funnel tube *B* sufficient water to cover the lower end of *B*, and then add sulphuric acid gradually until gas is evolved rapidly. In order to collect the gas over water a jar is filled with water, covered with a piece of wet cardboard, and inverted in the water in the pneumatic trough *D*. The jar is then placed over the hole in the shelf of *D*, and gas is passed by means of the delivery tube under the funnel, shown in section by *E*, when gas will rise and displace the water in the jar.
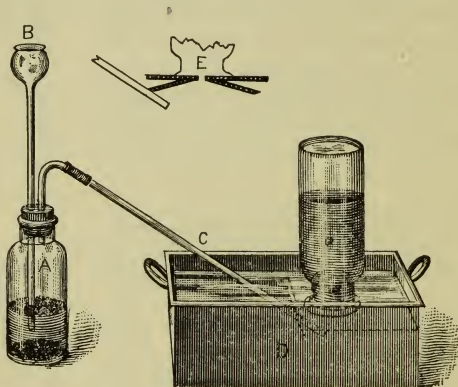

Fig. 52.

Fill a small jar with gas from the generator *A*. Remove the jar from the trough, holding it mouth downwards, and set fire to the gas. The result will probably be an explosion due to the air mixed with the hydrogen which was in the generator. Fill the jar again with hydrogen and ignite the gas. If it burns quietly it is sufficiently pure for further experiments.

Exp. **7**.—Allow hydrogen gas to escape from the delivery tube *C*, Fig. 52, into a dry jar. After a short time remove the jar, set fire to the gas at the end of *C*, and cover the flame with ano h ɪr dry bottle. Note observations. The yellow color of the hydrogen flame in this experiment is due to the sodium in the glass.

Exp. **8**.—Mix in a half-pint or pint jar 5 volumes of air and 2 volumes of hydrogen, and set fire to the mixture.

Exp. **9**.—Thrust a burning splinter of wood into a jar of hydrogen held mouth downwards.

The burning of hydrogen is one of the chemical properties of the element, and the change which occurs is chemical. It is better to study the nature of the reaction when we become familiar with oxygen, which unites with hydrogen to form water. Any substance which yields water when burned with air or oxygen contains hydrogen.

Exp. 10.—Fill two jars with hydrogen, leave one mouth uncovered upwards, and the other mouth downwards on the ring of a lamp-stand so that its mouth is not closed. After a few minutes apply a light to the gas in each bottle.

Exp. 11.—Fill a jar by holding it over a rapid current of hydrogen from the delivery tube C, Fig. 52, and prove that hydrogen has displaced the air which was in the jar.

Exp. 12.—Place a jar containing hydrogen over a similar one filled with air, and slowly invert the two. Apply a light to each. If successful, the gas in the jar which originally contained hydrogen will not burn.

Exp. 13.—Close the bowl of a white clay pipe with a disk of cardboard and sealing-wax. Connect the stem of the pipe with a narrow glass tube by means of rubber tubing. The apparatus is sufficiently tight if the tongue is held on the end of the tube after sucking air from the pipe. Place the end of the tube in water, and surround the pipe with a jar of hydrogen, and after a minute or two remove the jar. Observe whether gas bubbles through the water or the water rises in the tube, and note explanation of phenomena. Keep the pipe for future experiments.

Exp. 14.—Blow soap-bubbles with hydrogen, and hold a flame to some of the large bubbles.

Exp. 15.—When the evolution of hydrogen has ceased in the generator Exp. 6, Fig. 52, filter the solution into a porcelain dish, label it zinc sulphate, and set in the locker. The water will slowly evaporate, and after some days crystals will form, having the composition $ZnSO_4 + 7H_2O$.

THE SEVENTH GROUP.

The elements of this group are the non-metals chlorine, bromine, iodine, and fluorine, and the metal manganese.

Chlorine, Cl.

*Atomic Weight,* 35.5.   *Molecule,* Cl_2.

Chlorine occurs in nature only in combination with other elements. Its most abundant compound is common salt or sodium chloride.

It is a greenish-yellow gas about two and a half times heavier than air, having a density of 35.5 (hydrogen = 1). It condenses under cold and pressure to a yellow liquid, boiling at -- 33°.6. Chlorine gas dissolves in about half its bulk of cold water, forming a solution known as chlorine water.

Chlorine is obtained by several different methods. In the laboratory it is commonly prepared by warming manganese dioxide, MnO_2, with strong hydrochloric acid, which react as follows :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$

Chlorine gas is also prepared by heating a mixture of manganese dioxide, common salt, sulphuric acid, and water, whereby chlorine, manganese sulphate, hydrogen sodium sulphate, and water result :

$$MnO_2 + 2NaCl + 3H_2SO_4 = 2Cl + MnSO_4 + 2HNaSO_4 + 2H_2O.$$
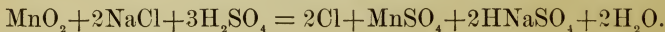
Exp. 16.—The flask *A*, Fig. 53, holds about a liter. Place in it 100 grams of pulverized manganese dioxide, 100 grams of common salt in coarse crystals, and a cooled mixture of 110 cc of strong sulphuric acid and 200 cc. of water. Much heat is evolved on mixing the acid and water, and there is danger of acid being thrown out of the vessel if water is poured into the acid. Hence the latter should be gradually added to the water. The wash-bottle *B* contains water to absorb hydrochloric acid gas, and *C* contains concentrated sulphuric acid to dry the
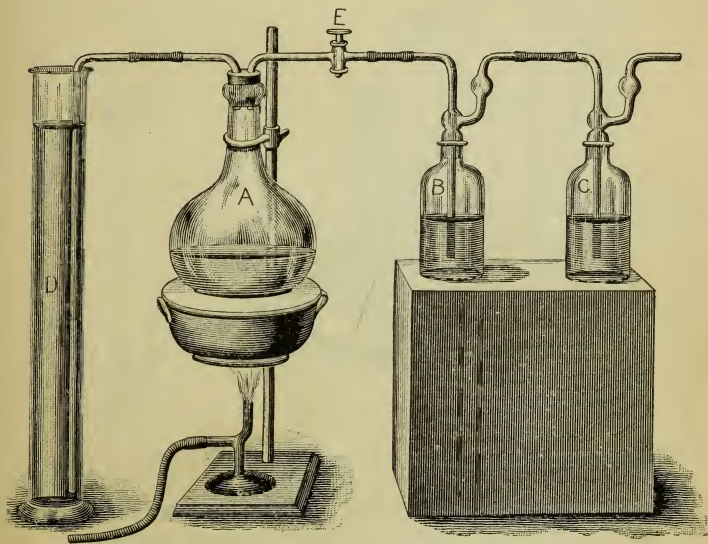

FIG. 53.

chlorine. A glass tube from *A* passes to the bottom of the cylinder *D*, containing a solution of potassium hydroxide to absorb any excess of chlorine. The glass stopcock *E* is to regulate the current of the gas. On gently warming the flask *A* by means of the water-bath, chlorine will come off regularly for a long time When the gas which passes from the bottle *C* is mostly absorbed by a solution of potassium hydroxide it is sufficiently free from air for use.

Fill glass-stoppered jars with chlorine by passing the gas to bottom of the jars until the color indicates that the air has been displaced by

the chlorine. Smear the stoppers with vaseline to make them gas tight. As chlorine is irritating and poisonous, experiments with it should be conducted under a good hood, or in such a way as to avoid inhaling the gas.

If it is not convenient to collect chlorine under a hood, the apparatus, Fig. 54, may be used. The plate contains lime water to absorb any chlorine which may escape on filling the jar under the bell-jar.
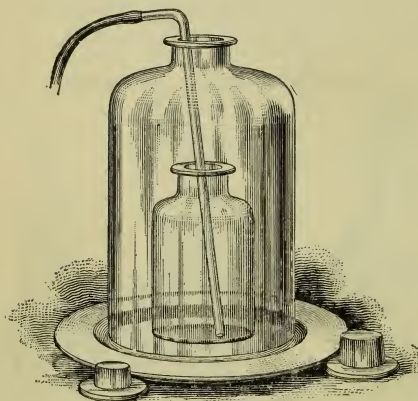

Fig. 54.   Fig. 55.

Exp. 17.—Ignite a small jet of hydrogen at the end of the glass tube, Fig. 55, tipped with a small tube made of platinum foil. Thrust the hydrogen flame into a jar of chlorine standing under the bell-jar (Fig. 54), and close the mouth of the latter with the rubber stopper A.

Exp. 18.—Set fire to a large jar of hydrogen, and introduce into it a jet of chlorine. The hydrogen will appear to support the combustion of the chlorine, while in the preceding experiment the chlorine appeared to be the supporter of the combustion. In either case the flame is due to the heat evolved by the union of the two gases, forming a compound described later.

Exp. 19.—*a.* Place in a cylinder, as shown in Fig. 56, a thin test-tube about 8 inches long and an inch in diameter, filled with water. Pass chlorine through the delivery-tube until the test-tube is half filled with the gas, and then pass in hydrogen until the test-tube is filled with the mixed gases, and remove the delivery-tube. The water will

slowly rise in the test-tube, and nearly fill it after some time, owing to the absorption of the product of the slow combination of the two gases.

b. Fill the tube again with equal volumes of chlorine and hydrogen, cover the top of the cylinder with a towel, and expose the mixed gases to bright sunshine or the light of burning magnesium, when a violent explosion will occur.

The foregoing experiments show that chlorine and hydrogen unite at high temperatures or when exposed to light. The compound formed contains both of these elements, and is called hydrogen chloride.

Let us next try to find the relative number of volumes of hydrogen and of chlorine which unite, and also the volume of the hydrogen chloride gas formed.
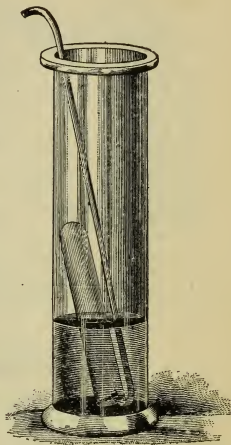

FIG. 56.

Exp. 20.—The apparatus, Fig. 57, is filled with a concentrated solution of hydrogen chloride in water, known as concentrated hydrochloric acid. The wires from a galvanic battery are connected with the gas-carbon poles. In one tube gas will be evolved rapidly. It is hydrogen, and hence will burn. At first but little gas will collect in the other tube, and on allowing it to escape into the air its odor will indicate that it is chlorine. After a time the acid will become saturated with chlorine, and on closing the stopcocks equal volumes of hydrogen and chlorine will be obtained.
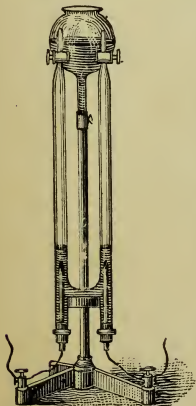

FIG. 57.

Exp. 21.—In order to obtain a mixture of equal volumes of hydrogen and chlorine, hydrochloric acid is subjected to electrolysis in some form of apparatus, such as shown by Fig. 58, in which the two gases are not separated. The apparatus consists of the tube *A*, with a rubber stopper, through which pass two gas-carbon sticks connected with wires from a battery by means of platinum wires. The neck of *A* passes through a cork

in a glass jar which serves as a stand. *A* is partly filled with
concentrated hydrochloric acid. A cur-
rent from 4 to 6 Bunsen cells will cause
a rapid evolution of the mixed gases,
and after the acid has become saturated
with chlorine a mixture of equal vol-
umes of hydrogen and chlorine will be
obtained. In order to protect the gases
from the action of sunlight the appa-
ratus may be placed in a box, the latter
being then filled with sawdust to in-
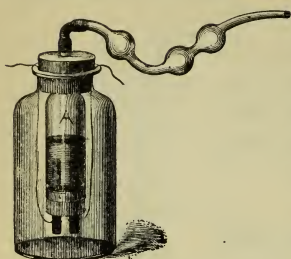sure complete exclusion of light.

Fig. 58.

Wrap the tube, Fig. 59, in black cloth,
and then pass through it the gases from the electrolysis of hydrochloric

Fig. 59.

acid until the air is expelled, taking pains not to expose the gases to
daylight. Close the stopcocks, and, without removing
the cloth, place the tube upright and allow one or two
cubic centimeters of a solution of potassium iodide to
flow in through the upper stopcock. Care should
be taken not to admit air. The chlorine will be ab-
sorbed by the potassium iodide and iodine liberated.
Finally, remove the cloth, open one stopcock under
water in a cylinder, and lower the tube until the re-
maining gas is under atmospheric pressure. The ex-
periment will demonstrate that half of the volume of
the mixed gases from the electrolysis of hydrochloric
acid is chlorine. The hydrogen remaining in the tube
may be burned.

Exp. 22.—Pass a mixture of equal volumes of hydro-
gen and chlorine through a tube, such as shown in Fig.
60, until the air has been displaced. Then close the upper
stopcock, disconnect the tube from the generator, and
quickly close the lower stopcock. Expose the tube to
bright sunshine or a magnesium light held near the
bulb. A slight click will indicate that the gases have
combined. Next, open one end of the tube under mercury. Gas
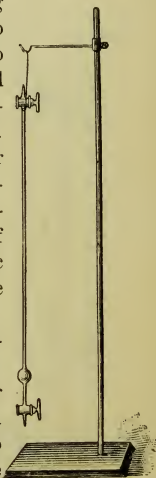
Fig. 60.

will not escape nor will mercury enter the tube, showing that the pressure of the gas in the tube is the same as before combination. Finally, fill one end of the tube beyond the stopcock with water, place under water, and open the lower stopcock. Water will absorb the gas quickly and fill the tube. The experiment shows that equal volumes of hydrogen and chlorine unite to form a compound (hydrogen chloride) which is soluble in water.

Molecules.—The combination of hydrogen and chlorine may be represented thus :

| Hydrogen. | Chlorine. | Hydrogen Chloride. |
| 1 Vol. | 1 Vol. | 2 Vols. |
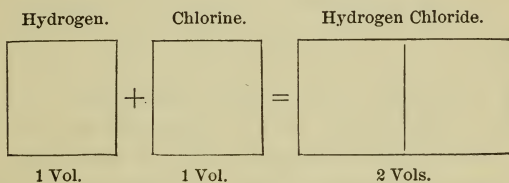
According to Avogadro's law, the two volumes of hydrogen chloride contain twice as many gas molecules as one volume of hydrogen. Since each molecule of the new gas contains both hydrogen and chlorine, it follows that in the reaction the molecules of both of these substances must have separated into two parts, each of the parts of the hydrogen molecule uniting with one of the parts of the chlorine molecule. Thus, since the experiment proves that the molecules of both substances are divisible, each kind of molecule must contain more than one atom. The simplest supposition is that each is composed of two atoms, but the combination can be equally well explained by supposing the hydrogen molecule to contain four or more atoms and the chlorine molecule an equal number. A consideration of the hydrogen chloride molecule and a comparison of it with the hydrogen molecule will be of service. Chlorine gas is 35.5 times heavier than hydrogen, and one volume of hydrogen weighing 1 unites with one volume of chlorine weighing 35.5 ; the atomic weights of the two are re-

spectively 1 and 35.5 : hence the hydrogen chloride molecule
consists of an equal number of atoms of each element.   It may
be represented by HCl, H_2Cl_2, H_3Cl_3, or a larger number of
atoms.   If it contain two or more atoms of hydrogen we should
expect to find some chemical changes in which only part of
the hydrogen is replaced.   On the contrary, all the hydrogen
of hydrogen chloride is replaced where the latter is acted upon
by metals.   From this chemical view we conclude that the
hydrogen chloride molecule contains but one atom of hydro-
gen and one atom of chlorine, and that it is represented by
the formula HCl.   If the hydrogen chloride molecule is HCl,
the hydrogen molecule is HH or H_2, as is evident from the
following reasoning.   Let us suppose one volume of hydrogen
to contain N molecules.   A like volume of chlorine will also
contain, according to Avogadro's law, N molecules, and the
two volumes of hydrogen chloride resulting from the combi-
nation of the two gases will contain 2N molecules of hydro-
gen chloride.   Each molecule of hydrogen chloride contains
one atom of hydrogen, and the 2N molecules contain 2N
atoms of hydrogen which were originally contained in N
molecules of hydrogen.   Hence each hydrogen molecule con-
tains two atoms and is represented by H_2.   The same argu-
ment leads to the conclusion that Cl_2 represents the chlorine
molecule.

The ratio of the weight of any gas molecule to that of the
hydrogen molecule is the ratio of the density of the gas to
that of hydrogen at the same pressure and temperature, as
has been shown, p. 38.   Since the smallest quantity of matter
which is known to act as an independent body in chemistry is
the atom of hydrogen, i.e. one half the hydrogen molecule,
it is convenient to choose that as the unit by which molecular
weights are measured ; hence we have the rule—

The molecular weight of any substance is equal to twice its
gas density.   •

Recalling again the union of hydrogen and chlorine :

Hydrogen.		Chlorine.		Hydrogen Chloride.	
1 Weight.	+	35.5 Weights.	=	18.25 Weights.	18.25 Weights.
1 Vol.		1 Vol.		2 Vols.	

The gas density of hydrogen chloride has been found by experiment to be 18.25. The molecular weight of hydrogen chloride is, therefore, 36.5. This corresponds to the weight of one atom of chlorine, plus the weight of one atom of hydrogen; thus, $35.5 + 1 = 36.5$.

The molecular weight of chlorine, according to the rule, equals 35.5, the gas density of chlorine, multiplied by 2 or 71, which is the weight of two atoms of chlorine. The molecule of chlorine is therefore Cl_2. The following rule requires no further explanation:

The number of atoms in a molecule of an element is found by dividing its molecular weight by its atomic weight.

Thus far we have taken for granted the atomic weight of chlorine. If we accept the conclusion arrived at from the consideration of the union of hydrogen and chlorine that the chlorine molecule contains two atoms, then the atomic weight of chlorine equals 35.5, or the molecular weight derived from the gas density of chlorine divided by 2. When we study the subject of atomic weights we shall have more complete reasons for regarding the atomic weight of chlorine as 35.5.

Molecular Weights of Compounds.—The molecular weight of a compound is twice its gas density, according to the rule previously stated. Since many compounds do not gasify without decomposing, or at temperatures too high to allow a determination of gas density, their molecular weights are unknown. In such cases it is customary to assign to a compound a formula representing the least mass which is sup-

posed to represent all the properties of the compound. Such formulas are often for convenience assumed to represent molecules.

Analysis, Synthesis.—A chemical analysis is the separation of a compound into its components ; as, for example, the separation of hydrochloric acid into hydrogen and chlorine. *Qualitative analysis* determines the constituents of a sub-stance, and the quantities or relative proportions of the several constituents are found by *quantitative analysis*. The *synthesis* of a compound is the uniting of the elements which compose it; as, for example, the combining of hydrogen and chlorine to form hydrochloric acid.

Chlorine unites with metals forming compounds termed chlorides. It combines energetically with hydrogen, removing the latter from many compounds with formation of hydrochloric acid.

Moist chlorine is a powerful bleaching agent, but the dry gas has ordinarily no effect on coloring matters. The bleaching action of chlorine is due, wholly or in part, to the withdrawal of hydrogen from water, setting free oxygen which oxidizes or destroys the colored compounds. Oxygen in the ordinary state does not act as a bleaching agent. If, however, it is in the *nascent* state, i.e., when the atoms of this element are just set free from compounds, it is more active chemically, and will bleach coloring matter. Later we shall learn that the molecules of ordinary oxygen contain two atoms. The atoms of oxygen in the nascent state are supposed to be free, having a marked tendency to combine with other substances present, or with each other.

The following equation represents the action of chlorine on

water, one atom of oxygen being set free from one molecule of water:

$$H_2O + Cl_2 = 2HCl + O.$$
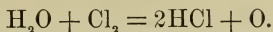
Chlorine gas is a good disinfectant, destroying germs and the noxious compounds of decay.

Exp. 23.—*a.* Place some Dutch leaf (an alloy of copper and zinc beaten into thin sheets) in a pint jar of chlorine.

b. Drop some pulverized metallic antimony into chlorine.

Exp. 24.—Place a dry piece of phosphorus on a deflagrating spoon made of chalk and copper wire, and thrust into chlorine.

Exp. 25.—Fill a large thin glass tube, closed at one end, with a saturated solution of chlorine in water, and place the open end of the tube in a jar containing some chlorine water, taking care that no air enters the tube. Set the apparatus in bright sunshine. After a time minute bubbles of gas will be seen, and in course of a day sufficient gas will collect in the tube to test. The gas thus obtained is oxygen, and will cause a glowing splinter of wood to inflame and burn when thrust into it.

Exp. 26.—Saturate a piece of thin filter-paper held by a wire with boiling turpentine, and quickly plunge into a jar of chlorine. The turpentine will inflame. It is a compound of carbon and hydrogen. The latter unites with the chlorine, and the carbon is separated as soot.

Exp. 27.—Leave a piece of dry pink calico in a stoppered jar of dry chlorine for an hour or longer. Then add a little water. Note the results.

Exp. 28.—Place in chlorine water pieces of calico, printed paper, and paper with lead-pencil and writing-ink marks. Printing-ink contains lamp-black, a form of carbon, and the lead of a lead-pencil is chiefly graphite, another modification of carbon. Free carbon is not attacked by chlorine.

Exp. 29.—To a few drops of a solution of silver nitrate in a test-tube add some chlorine water. The white precipitate obtained is silver chloride, AgCl.

The term *precipitate*, which means literally something thrown down, is applied to solids which separate when two solutions are mixed.

Exp. 30.—Dissolve a little common salt (sodium chloride, NaCl) in water and add to the solution silver nitrate. Also add silver nitrate to very dilute hydrochloric acid. In both cases silver chloride will be

5

precipitated. The experiments show that silver nitrate may be used to detect chlorine, but later we shall learn that a few other substances, less common than chlorine, also yield white precipitates with silver nitrate.

Hydrochloric Acid or Hydrogen Chloride, HCl, is a colorless gas, very soluble in water. The solution is commonly known as hydrochloric or muriatic acid. One volume of water at 0° absorbs 503 volumes of the gas at 760 mm. pressure. At ordinary temperatures about 450 volumes are absorbed, forming a solution having a density of about 1.2, and containing approximately 40 per cent of hydrogen chloride. A concentrated solution of the acid fumes strongly in the air, and on heating gives off hydrochloric acid gas, the temperature of the liquid rising to 110°, when an aqueous acid containing 20.24 per cent of HCl distils unchanged at 760 mm. pressure. A more dilute acid loses water on boiling until it attains the same strength. The observed density of hydrochloric acid gas is 18.25 (hydrogen = 1).

Hydrochloric acid is made in enormous quantities by heating a mixture of common salt and sulphuric acid, and absorbing the gas by water.

In the reaction hydrochloric acid and hydrogen sodium sulphate are formed, thus:

$$(1) \quad NaCl + H_2SO_4 = HCl + HNaSO_4.$$
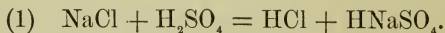
If sufficient salt is taken and the mixture more strongly heated, the hydrogen sodium sulphate reacts with the salt as follows:

$$(2) \quad HNaSO_4 + NaCl = HCl + Na_2SO_4.$$

The hydrogen sodium sulphate of the first reaction is more readily soluble in water than the sodium sulphate obtained by the second reaction.

How many grams of hydrogen chloride can be made from 50 grams of sodium chloride, and how much sulphuric acid will be required if the salt and acid are used in the proportion required by the first equation?

Exp. 31.—Place 100 grams of coarse crystals of common salt in a flask having a capacity of a liter, and pour in a cool mixture of 100 cc. of concentrated sulphuric acid and 25 cc. of water. Connect the flask with
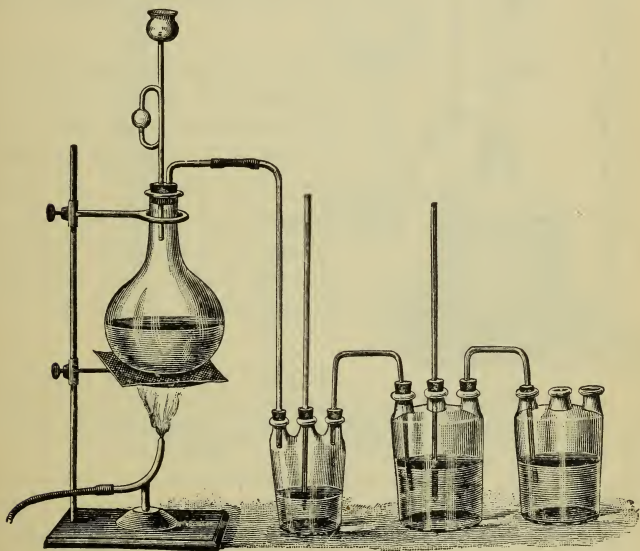

FIG. 61.

three Woulfe bottles, Fig. 61, containing water. Heat the flask gently with a lamp as long as gas is freely evolved. Test the liquid in each bottle with blue litmus paper.

Exp. 32.—The apparatus shown in Fig. 62 may be used to illustrate the rapid absorption of hydrochloric acid gas by water. The strong glass globe A is filled by passing a rapid current of hydrochloric acid gas into it for 15 or 20 minutes. The bottle B contains water colored

blue with a solution of litmus.   Open the pinchcock D, and blow into the tube C for an instant, to force the water into A.
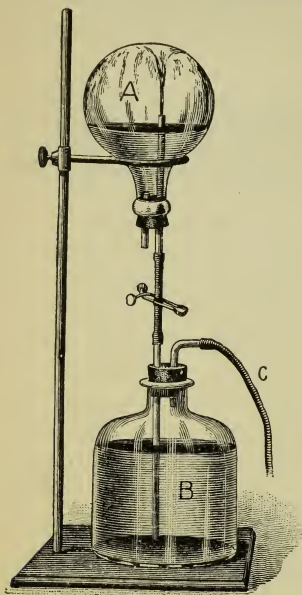
Exp. 33.—Fill the cylinder A, Fig. 63, with gas obtained by heating fuming hydrochloric acid contained in the flask B.   When acid fumes escape freely from the cylinder remove the delivery-tube, and quickly place the mouth of the cylinder under water.   The hole in the cork C is about twice the diameter of the delivery-tube passing through it.

FIG. 62.

The composition and physical properties of hydrochloric acid have been considered, while as yet but few of its chemical properties have been noticed.   Its acidic character and deportment towards a class of compounds known as bases can best be made evident by the following experiments :

Exp. 34.—Dilute a few drops of hydrochloric acid with a test-tube full of water.   Taste a drop of the very dilute acid, and also try the action of it on blue litmus paper.

Exp. 35.—Take a stick of sodium hydroxide about two inches long, notice its action on the fingers, and then dissolve it in a test-tube half full of water *without applying a lamp flame.*   Cool the solution by placing the test-tube in cold water.   Dilute a few drops of the solution largely with water, taste, and test with litmus paper reddened with very dilute acid. Pour one third of the original solution of sodium hydroxide into another test-tube, and add to it some hydrochloric acid.   The rise in temperature indicates that a change has occurred.   Transfer the solution to a porcelain dish, and add to it most of the original solution of sodium hydroxide. Then add hydrochloric acid to the contents of the dish until the solution does not change the color of a red or a blue litmus paper.   When this is attained, the acidic properties of the hydrochloric acid and the basic

properties of the sodium hydroxide used have disappeared. The acid and base have mutually neutralized each other. The taste of the solution shows that it contains common salt. Filter the solution, and evaporate slowly over a lamp until a dry residue remains. If a solution of
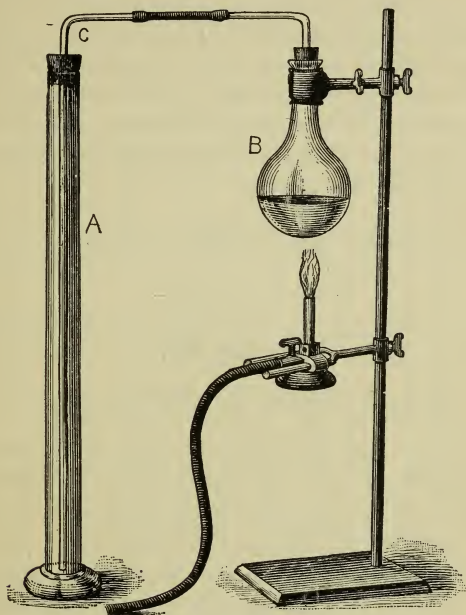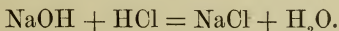

Fig. 63.

the salt is allowed to evaporate at ordinary temperature crystalline cubes will be obtained.

The chemical change in which common salt, NaCl, is formed from sodium hydroxide, NaOH, and hydrochloric acid is represented by the equation—

$$NaOH + HCl = NaCl + H_2O.$$

H_2O is a molecule of water formed in the reaction. The water

which held the acid and base in solution served as a medium in which the changes occurred, but did not take part in them, and hence is not represented in the equation. The hydrogen of the hydrochloric acid has been exchanged for sodium, or, as more commonly expressed, has been replaced by sodium. When metallic zinc dissolves in hydrochloric acid the hydrogen replaced escapes as a gas. If a compound of zinc and oxygen known as zinc oxide, ZnO, is dissolved in hydrochloric acid the hydrogen of the acid is replaced as before by the zinc, but instead of escaping, unites with the oxygen of the zinc oxide to form water, thus:

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$
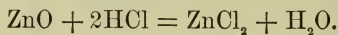
Bromine, Br.

Atomic Weight, 80.   *Molecule,* Br_2.

Bromine is not found in the free state in nature, but always in combination with metals. It exists in small quantities in many salt springs and in sea water. A considerable part of the bromine in commerce is obtained from salt springs in West Virginia. Bromine is a dark-red volatile liquid, freezing at $-24°.5$ and boiling at $63°$. The density of liquid bromine is 3.18 at $0°$. The gas density of bromine at $100°$ is 80, while at about $1500°$ it has been found to be 57 to 67, showing that diatomic bromine molecules dissociate at high temperatures. The calculated gas density of a mixture of equal molecules of Br_2 and Br_1 is 60.

Bromine is very soluble in chloroform, and is soluble in 30 parts of water.

Exp. 36.—Drop a thin glass bulb containing a few cubic centimeters of bromine into a tall cylinder, and cover the cylinder with a ground-glass plate. The vapor of bromine, though over five times heavier than air,

will soon rise to the top of the cylinder. In handling bromine care should be taken to avoid inhaling its vapor, as it is poisonous, and very irritating. Liquid bromine is corrosive to the skin.

Exp. 37.—Shake up bromine and water in a stoppered bottle to make bromine water.

Bromine may be obtained from bromides by the action of manganese dioxide and sulphuric acid in the same way that chlorine is obtained from sodium chloride. In chemical deportment bromine resembles chlorine, uniting with metals to form bromides analogous to the chlorides. It combines with hydrogen to form hydrobromic acid, but the union does not take place in sunlight, as is the case with chlorine and hydrogen. If hydrogen mixed with bromine vapor is burned in the air a small quantity of hydrobromic acid will be formed.

Hydrobromic Acid or Hydrogen Bromide, HBr, is a colorless gas, very soluble in water. It cannot well be made by acting on bromides with sulphuric acid, owing to its decomposition by sulphuric acid with separation of bromine. It is best prepared by adding bromine to red phosphorus and water, when the following reaction occurs:

$$P + 5Br + 4H_2O = 5HBr + H_3PO_4.$$
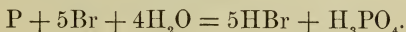
The gas is passed through a tube containing red phosphorus to free it from bromine vapor.

Iodine, I.

*Atomic Weight,* 127. *Molecule,* I_2.

Iodine occurs sparingly in nature. It is found in salt beds and springs in minute quantities. It cannot be profitably extracted from sea water, but certain sea weeds take it from the water, and from their ashes or kelp iodine is obtained. The

mother-liquors of Chili nitre, $NaNO_3$, are also a source of iodine.

Iodine is an almost black crystalline solid, with a metallic lustre, having a density of 4.95 at 17°. It melts between 113° and 115°, and boils above 200°. Its vapor when pure appears deep blue by transmitted light, but when mixed with air it has a reddish-violet color. Iodine volatilizes slowly at ordinary temperature, and its odor is similar to but feebler than that of chlorine and bromine. Iodine is soluble in chloroform, in a solution of potassium iodide, and in alcohol, but is almost insoluble in water.

The gas density of iodine below 500° is 127, corresponding to the molecule I_2. With increasing temperature the density diminishes, and above 1500° it has been found to be 65.7 ; the calculated density of molecules of I_1 is 63.5. The diatomic molecules of iodine dissociate at a sufficiently high temperature into monatomic molecules.

Iodine forms compounds analogous in composition and properties to chlorine and bromine compounds. It unites with metals to form iodides. Chlorine and bromine displace iodine from metallic iodides ; for example—

$$KI + Cl = KCl + I.$$
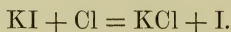
The characteristic reaction of iodine is the blue color it imparts to starch-paste. Combined iodine, however, does not blue starch.

Exp. 38.—Place a few crystals of iodine in a dry test-tube, and warm in lamp flame until iodine vapor fills the tube ; observe the color, and allow to cool. Small crystals will be formed on the sides of the tube. Next add water, and heat to boiling. Notice whether iodine escapes with the steam. Preserve the aqueous solution for further experiments.

Hydriodic Acid or Hydrogen Iodide, HI, is a colorless gas similar in properties to hydrogen chloride and hydrogen bromide. Iodine and hydrogen unite when passed over hot

platinum sponge, but practically hydrogen iodide is obtained
by the reaction which occurs between phosphorus, iodine,
and water :

$$P + 5I + 4H_2O = 5HI + H_3PO_4.$$
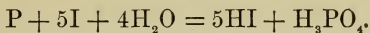
Hydrogen iodide is very soluble in water, the solution
saturated at 0° having a density of 1.99. The aqueous solu-
tion is colorless, but soon reddens on exposure to air and light,
owing to separation of iodine. Hydrogen iodide is readily
decomposed by heat. The influence of a small amount of
matter on a compound is well illustrated by hydriodic acid
containing in 128 parts only 1 part of hydrogen. Hydrogen
iodide gas is decomposed by mercury, hence it can only be
collected by displacing air.

Exp. 39.—Place in the retort, Fig. 64, a few grams of red phosphorus,
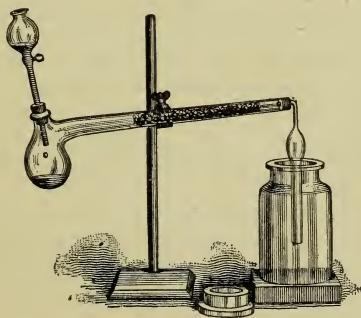and drop in slowly by means of the tap funnel a solution of 2 parts of

FIG. 64.

iodine in 1 part of hydriodic acid of density 1.7. Hydrogen iodide will
be evolved without application of heat at first; later, gentle warming
will be necessary. To free the gas from iodine vapor, moist red phos-
phorus is placed with a loose filling of asbestus in the neck of the
retort. Fill two or three glass-stoppered jars with the gas ; then pass
the gas into water contained in a test-tube standing in a jar of cold
water. Preserve the solution for future use.

Exp. 40.—*a.* Pour hydrogen iodide gas from a jar on a large Bunsen flame. The gas will be decomposed by the heat, and a brilliant cloud of iodine will be seen. *b.* Allow a colorless solution of hydrogen iodide to stand in light to find if decomposition occurs.

Iodine Monochloride, ICl, and Iodine Trichloride, ICl_3.— When dry chlorine is passed into a jar containing iodine, a dark-brown liquid results, from which ICl crystallizes on cooling. With an excess of chlorine, lemon-yellow crystals of ICl_3 form, which give off chlorine at 25°, leaving the monochloride.

Exp. 41.—To a granule of potassium bromide in a test-tube add considerable chlorine water. The change in color will indicate that bromine is set free:

$$KBr + Cl = KCl + Br.$$
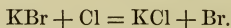
Add to the solution a few drops of chloroform, and shake violently. Note observations.

Exp. 42.—Add chlorine water gradually to a small granule of potassium iodide. The first portions of iodine set free will dissolve in the solution of potassium iodide, and when sufficient chlorine water has been added a black precipitate of iodine will separate, since iodine is nearly insoluble in a solution of potassium chloride.

Exp. 43.—Dissolve a few crystals of iodine in a little alcohol, and place some of the solution on the hand. The stain may be removed by ammonia water.

Exp. 44.—Place in half a test-tube of water not more starch than can be taken up on the end of a penknife blade; shake thoroughly, and heat to boiling, with frequent shaking to avoid burning the starch on the bottom of the tube. The starch granules burst in warm water, and a thin, translucent starch-paste will result.

Add a few drops of starch-paste to chlorine water, bromine water, and iodine water in separate test-tubes, and note any changes. To the tube containing iodine add an excess of chlorine water.

Exp. 45.—Dilute a few drops of solution of potassium iodide* with

---

* Experience has shown that a solution of potassium iodide which has stood for a time in a laboratory is liable to contain free iodine. The instructor should test the solution beforehand, and, if it reacts for iodine, he may cautiously add potassium hydroxide until no reaction for iodine appears on testing with starch-paste.

water, and add a little starch-paste. Note change, if any; then add a drop of chlorine water, and finally sufficient chlorine water to remove color.

Exp. 46.—To a solution of potassium bromide and starch-paste add chlorine water.

Exp. 47.—To a very dilute solution of potassium iodide containing starch-paste add a little and then an excess of bromine water.

Represent by equations the reactions in the foregoing experiments in which chlorine liberates bromine and iodine, and in which bromine liberates iodine. Chlorine, iodine and water react to form iodic acid, HIO_3:

$$I + 5Cl + 3H_2O = HIO_3 + 5HCl.$$
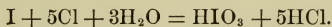
This explains why an excess of chlorine discharges the blue color of iodine and starch, as iodic acid does not color starch blue.


Fluorine, F.

Atomic Weight, 19.   *Gas Molecule unknown.*

Fluorine occurs combined with calcium as fluor spar or fluorite, CaF_2, which is abundant in some localities. It is also a constituent of cryolite, $3NaF + AlF_3$, found in Greenland, and of several other minerals. Sea water and the waters of many mineral springs contain it, and it has been found in the teeth and other parts of the body.

Fluorine resisted many attempts to isolate it until the year 1886, when Moissan succeeded in electrolyzing anhydrous hydrogen fluoride kept at a low temperature, and obtained free fluorine as a colorless gas. It combines explosively with hydrogen in the cold, and sets free chlorine from cold potassium chloride. Crystallized boron and silicon, arsenic, antimony, sulphur, and iodine burn brilliantly in fluorine gas. The metals also burn in it, but less violently. Cork chars and ignites in the gas, and alcohol, benzene, and turpentine are inflamed by it. It decomposes water with formation of hydrogen fluoride and ozone.

Hydrofluoric Acid or Hydrogen Fluoride, HF and H_2F_2. — Hydrogen fluoride is a colorless liquid, boiling at $19°.5$, and solidifying at $-102°.5$ to a transparent crystalline mass, which melts at $-92°.3$. Its gas density at $30°.5$ has been found to be 19.66, showing that at this temperature the molecule is H_2F_2. At higher temperatures the density of the gas is about 10, corresponding to the molecule HF. Hydrogen fluoride mixes in all proportions with water. Care is necessary in experimenting with hydrofluoric acid, as it is very poisonous when inhaled, and when pure or in very concentrated solution blisters the skin, producing sores which heal slowly. A dilute aqueous solution does not attack the skin. Anhydrous hydrofluoric acid is without action on glass, but if a trace of water is present it corrodes glass. The aqueous acid dissolves glass, thus differing in this respect from all other acids. The acid does not attack gold, platinum, or silver, and the concentrated aqueous solution of it may be kept for several years in a leaden jug, which, however, will slowly be corroded. Gutta-percha bottles are used for holding it, but in time they crack. The dilute hydrofluoric acid of commerce is transported in wooden casks.

Hydrofluoric acid is used in the laboratory as a solvent, and in the arts both the gas and its solution are used for etching glassware. The anhydrous acid is best prepared by heating hydrogen potassium fluoride, HFKF, in a platinum retort, and condensing the vapors in a platinum vessel immersed in a freezing mixture. The common method of making hydrofluoric acid is by heating fluor spar, CaF_2, with concentrated sulphuric acid, when hydrofluoric acid and calcium sulphate are produced :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
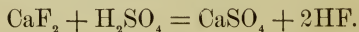
Nearly anhydrous acid distils, which may be collected in a cooled receiver, or conducted into water if an aqueous solution is desired.

Exp. 48.—Cover the convex side of a small watch-glass with a thin coating of melted beeswax, and, when cool, mark lines through the wax, thus exposing the glass. Place a thimbleful of powdered fluor spar in a leaden cup, add sufficient sulphuric acid to make a thin paste, and heat cautiously with a small flame until fumes appear on holding the stopper from the ammonia bottle over the dish. Place a cardboard ring on the cup to keep the warm metal from contact with the wax, and on the ring put the watch-glass, with the wax side exposed to the fumes. Pour a little ammonia water into the watch-glass to keep the wax from melting, and also to combine with any acid which may escape. After half an hour remove the wax from the glass by warming, and then rubbing with a piece of paper.

Exp. 49.—Coat a tube with wax, and graduate it to millimeters. Then cover the graduation with a strip of thin filter paper, and moisten the paper with strong, but not fuming, hydrofluoric acid by means of a camel's-hair brush. In a short time the etching will be completed.

Summary of the Halogens.

Fluorine, chlorine, bromine, and iodine are known as the halogens (salt producers), as they all form with metals compounds analogous to sea salt, $NaCl$. They constitute, together with manganese, the seventh group of the periodic system. Manganese is a metal like iron in many respects, and possessing few characteristics common to the group. The halogens are a well-defined group of elements, exhibiting close analogy in their chemical deportment. They unite with hydrogen to form the compounds HF, HCl, HBr, and HI, all of which are strong acids. The sodium and potassium halides are NaF, $NaCl$, $NaBr$, NaI, KF, KCl, KBr, and KI. The halogens in their analogous compounds present a gradation in the energy with which they enter into combination, corresponding to the differences of their atomic weights. Fluorine, with the lowest atomic weight, combines with hydrogen at common temperature ; chlorine under the influence of light or heat ; bromine, less readily ; and iodine, with the highest atomic weight

scarcely combines directly with hydrogen. Fluorine displaces chlorine from potassium chloride, and presumably bromine and iodine from potassium bromide and iodide. Chlorine displaces bromine and iodine, and bromine displaces iodine. Fluorine decomposes water rapidly, chlorine slowly, under the influence of light, and bromine has little and iodine no action upon water. Hydrogen iodide in aqueous solution decomposes readily, hydrogen chloride in concentrated solution is slightly decomposed by long exposure to light, while hydrogen fluoride is unchanged. The following table shows a gradation of physical properties with increasing atomic weights :

	Atomic Weight.	Gas Density.	Color.	Melting point.	Boiling point.
Fluorine.....	19	....	Colorless.	....	....
Chlorine.....	35.5	35.5	Greenish yellow.	....	— 33°.6
Bromine.....	80	80	Red.	— 24.5	63°
Iodine.......	127	127	Black.	113	above 200°

Manganese, Mn.

Atomic Weight, 55.   *Density*, 8.

Pyrolusite, or black oxide of manganese, MnO_2, and manganite, $Mn_2O_3 + H_2O$, are the chief ores of manganese. It occurs in many minerals, and has been found in small quantities in animals and plants.

Metallic manganese is obtained by reducing the oxides by means of carbon at a white heat. The pure metal is hard, brittle, and has a grayish-white lustre. It oxidizes in air, decomposes hot water, and dissolves in acids. Impure manganese, containing iron, carbon, and silicon, is not affected by air.

Manganous Chloride or Manganese Dichloride, $MnCl_2$, results from the direct union of its elements. A solution of the

salt is prepared by dissolving any of the oxides of manganese in hot concentrated hydrochloric acid. The solution on cooling or spontaneous evaporation deposits pink crystals of $MnCl_2 + 4H_2O$, which lose two molecules of water in dry air, and deliquesce in moist air. The salt is very soluble in water, and readily soluble in alcohol.

The compounds $MnBr_2$, MnI_2, and MnF_2 are easily obtained.

Manganese Tetrachloride, $MnCl_4$, has not been isolated. Manganese dioxide, MnO_2, dissolves in cold concentrated hydrochloric acid. It is supposed that the tetrachloride is formed as follows :

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$
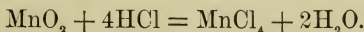
The dark-brown solution soon decomposes, and for each molecule of MnO_2 two atoms of chlorine are set free, manganese dichloride remaining in the solution.

Manganese Tetrafluoride, MnF_4, has been obtained in combination with potassium fluoride as $2KF.MnF_4$.

VALENCE.

WE have seen that there are good reasons for supposing the molecule of hydrogen chloride to be composed of one atom of hydrogen and one of chlorine, and represented by the formula HCl. Later we shall learn that there are equally good reasons for regarding the molecule of water as H_2O, that of ammonia as H_3N, and that of methane as H_4C. These four compounds show that chlorine, oxygen, nitrogen, and carbon differ in their power to hold in combination atoms of hydrogen. Chlorine unites with one, oxygen with two, nitrogen with three, and carbon with four atoms of hydrogen. The four compounds named illustrate the general fact that the atoms of every element possess the power of holding in combination one or more atoms. This property is termed *valence*, and may be defined thus :

The valence of an atom is its capacity to hold in combination other atoms or groups of atoms (compound radicals).

Hydrogen never appears to possess a valence greater than one, and is therefore taken as a measure of valence. Most elements do not combine with hydrogen alone, and their valence is measured in their combinations with elements whose valence is measured by hydrogen. Silver, for example, does not unite with hydrogen, but unites with chlorine in the proportion of one atom to one atom, and is therefore regarded as having a valence equal to that possessed by an atom of hydrogen.

Valence is expressed by calling hydrogen and chlorine univalent or monads, oxygen bivalent or a dyad, nitrogen trivalent or a triad, and carbon tetravalent or a tetrad. For higher

valences we have the terms pentavalent or pentad, hexvalent
or hexad, and heptavalent or heptad. Valence is indicated
by Roman numerals or bars attached to symbols, thus:
$\overset{\text{II}}{\text{O}}$ or $-\text{O}-$. Water is represented by H–O–H, ammonia by

$\overset{\text{H}}{\underset{\text{H}}{\text{H}}}{>}\text{N}$, methane by $\overset{\text{H}}{\underset{\text{H}}{\overset{\text{H}}{\underset{\text{H}}{}}}}{>}\text{C}$, or H–C–H. These are termed

graphic formulas. The bars represent what is often vaguely
called bonds or units of affinity. Thus we say that chlorine
possesses one, oxygen two, nitrogen three, and carbon four
bonds. The graphic formulas above are not intended to in-
dicate the positions of the atoms in the molecules, but simply
their valence, and the relations the atoms bear to each other.

In the case of chlorine, oxygen, nitrogen, and carbon their
valence is measured by the number of atoms of hydrogen which
combine with each. When we consider molecules composed
of two elements, each of which exhibits towards hydrogen a
valence greater than one, we find, according to our definition,
that an element may have a valence differing from that shown
in its compound with hydrogen. For example, the molecule
of carbon dioxide contains one atom of carbon and two atoms
of oxygen. Assuming that both atoms of oxygen bear the
same relation to the atom of carbon, we may write the graphic
formula thus: O–C–O, in which carbon is a dyad. Philo-
sophically there is as much reason to regard carbon as a dyad
in carbon dioxide as there is to consider it a tetrad in methane.
There is, however, this practical objection to viewing carbon
as a dyad in carbon dioxide—the formula O–C–O does not
exhibit the same valence of oxygen and carbon which appears
in the hydrogen compounds. But by indicating the valence
each element possesses, measured by hydrogen, by the formula
O=C=O, we have the same valence for carbon in carbon

6

dioxide as in methane, and also represent the atom of oxygen as equivalent to two atoms of hydrogen.

The halogens towards hydrogen and the metals are mo-

nads, as in H–Cl, H–Br, H–I, H–F, Na–Cl, K–Cl, and

$Mn <^{Cl}_{Cl}$.   Iodine, however, exhibits a higher valence in iodine

trichloride, $I <^{Cl}_{-Cl} _{Cl}$ This is an illustration of one of the chief

difficulties in the hypothesis of valence, namely: that the valence of an element may vary, or is only shown in certain compounds. Some authorities regard true valence as the greatest capacity of an atom to hold in combination other atoms. Since a chemical compound results from the mutual relations of the elements composing it, we may say that the valence exhibited also depends upon the mutual relations of its elements. According to this view, an element may exhibit a variable valence, as illustrated in case of iodine. Other difficulties in the imperfect hypothesis of valence cannot be profitably discussed now. The hypothesis has been, and is, of great service in classifying and formulating compounds. It is also a help in studying chemistry, and therefore it has been taken up before the student has become familiar with a large number of compounds, a knowledge of which is necessary in order to understand a more complete discussion of the subject. We shall hereafter in this book use the hypothesis of valence, and use graphic or constitutional formulas for many compounds, more especially for the more common ones.

THE FIRST GROUP.

THE members of this group are the alkali metals, and copper, silver, and gold. The alkali metals, so called because their hydroxides are strong alkalies, are lithium, sodium, potassium, rubidium, and cæsium. They are all light metals, with low melting points; while copper, silver, and gold have high densities and high fusing points. All of the elements of the first group unite with the halogens atom for atom; as, for example, $LiCl$, $NaCl$, KCl, $RbCl$, $CsCl$, Cu_2Cl_2, $AgCl$ and $AuCl$. There are also the chlorides $CuCl_2$, $AuCl_2$ and $AuCl_3$.

The Alkali Metals.

	Atomic Weight.	Density.	Atomic Volume.	Melting point.
Lithium.........	7	0.59	11.9	180°
Sodium..........	23	0.97	23.7	95.6
Potassium.......	39.1	0.87	45.5	62.5
Rubidium.......	85.5	1 52	56.2	38.5
Cæsium..........	133	1.88	70.7	26.5

The alkali metals constitute a well-defined natural group. They all decompose water rapidly at common temperature, liberating hydrogen, and quickly tarnish in air. They combine with the halogens to form compounds containing one atom of metal to one atom of halogen, and are therefore monads. We have seen that the halogens are strongly acidic, and shall shortly learn that the alkali metals are strongly basic. They are, in fact, the most basic elements known. Potassium, rubidium, and cæsium have chemically the closest

resemblance. Lithium approaches in some properties the metal magnesium of the second group. Sodium is intermediate in properties between potassium and lithium.

The physical properties of the alkali metals vary with their atomic weights. Thus their densities and atomic volumes increase with their atomic weights, while the melting points diminish, as shown in the foregoing table.

Atomic Volume.—The quotients obtained by dividing the atomic weights by the densities (water = 1) of the elements in the solid form are called atomic volumes. They represent the relative volumes occupied by atomic quantities in the solid form. Thus the atomic volume of lithium is $7 \div 0.59 = 11.9$; of cæsium it is $133 \div 1.88 = 70.7$. In other words, 7 grams of lithium measure 11.9 cc., and 133 grams of cæsium measure 70.7 cc.

Lithium, Li.

Atomic Weight, 7.   Density, 0.59.

Lithium was discovered in 1807 by Arfvedson. A number of minerals contain a few per cent of it, and a larger number contain traces of it. It is widely distributed in the animal and vegetable kingdoms, and is found in sea, river, and spring waters. It has been detected in meteorites.

Metallic lithium is obtained by decomposing the molten chloride with the current from four to six cells of a Bunsen battery. The metal cannot be prepared by heating the carbonate with charcoal.

Lithium possesses the lustre of silver, is softer than lead, but harder than sodium. It tarnishes on exposure to air, but not so readily as sodium and potassium. It is the lightest known solid. The lithium compounds impart an intense red color to the flame, but the metal itself burns in air with a

brilliant white light. Lithium attacks glass, porcelain, and silica below 200°.

Lithium Chloride, LiCl, is formed when the metal burns in chlorine, and when lithium carbonate is dissolved in hydro-chloric acid. The anhydrous chloride separates on evaporating a solution of the salt above 15°.5. At temperatures below 10° lithium chloride crystallizes with water, forming the hydrate $LiCl + H_2O$, or $LiCl + 2H_2O$. Lithium chloride is very soluble in water and alcohol, and is very deliquescent.


Sodium (Natrium), Na.

Atomic Weight, 23. *Density,* 0.97.

The most abundant compound of sodium is common salt. Sodium is very widely distributed, occurring in all soils, many minerals, and in animals and plants. It is so commonly present that it is difficult to obtain substances in which the spectroscope will not show traces of it.

Metallic sodium possesses a silver-white lustre, is ductile at 0°, and soft at ordinary temperature, and melts at 95°.6. It is volatile at a red heat, but attempts to determine its gas density have not given satisfactory results, owing to the fact that the metal attacked the containing vessels at high temperatures. Sodium was first isolated by Davy in 1807, by the electrolysis of sodium hydroxide.

The metal is now manufactured by reducing sodium carbonate with coal at an intense heat ; sodium distils from the retort, and its vapor is condensed in a suitable receiver. The reaction is as follows :

$$Na_2CO_3 + 2C = 2Na + 3CO.$$
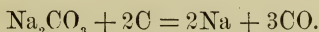
In a new process, said to give a better yield, an intimate mixture of finely divided iron and charcoal are substituted for coal.

Sodium does not oxidize in perfectly dry air, but tarnishes quickly when a fresh surface is exposed to ordinary air, and the metal is slowly but completely corroded. Hence it must be preserved from the air either in petroleum oil, by a coating of paraffine, or in closed vessels. When the metal is placed in hot water the escaping hydrogen is inflamed by the heat of the reaction. The decomposition of water by sodium at ordinary temperature has already been noticed. The metal does not lose its lustre in perfectly dry chlorine gas, but if the latter is moist, sodium chloride is found.

Sodium Chloride, Common Salt, NaCl or Na–Cl, is obtained from sea water, salt springs, and salt mines. The salt of commerce is in the form of a fine crystalline meal, such as the fine table and dairy salt ; in coarse crystals which form on slow evaporation of brine, and in large lumps which come from the salt mines. Sodium chloride crystallizes in transparent cubes, having a density of 2.16. It is but little more soluble in hot than in water of ordinary temperature, as shown by the following table giving the quantities of sodium chloride which are dissolved by 100 parts of water at different temperatures :

Temperature.	0°	14°	40°	80°	100°
NaCl..........	35.5	35.9	36.6	38.2	39.2

The hydrate $NaCl + 2H_2O$ separates on cooling a saturated solution of salt to $-10°$, and on lowering the temperature to $-22°$ crystals of $NaCl + 10H_2O$ form. Sodium chloride fuses at 776°, and at higher temperatures volatilizes.

The common salt of commerce contains small quantities of sodium and calcium sulphates and magnesium chloride. The latter renders salt liable to become damp in the air.

Pure sodium chloride may be obtained by passing hydrochloric acid gas into a saturated solution of common salt. Sodium chloride will separate, and may be washed with con-

centrated hydrochloric acid and then dried. The impurities will remain in solution.

Exp. 50.—To illustrate the insolubility of sodium chloride in hydrochloric acid add the concentrated acid to a saturated solution of salt.

The other sodium halides are *Sodium Fluoride*, NaF ; *Sodium Bromide*, NaBr ; and *Sodium Iodide*, NaI.

Potassium (Kalium), K.

Atomic Weight, 39.1.   *Density,* 0.87.

Potassium is widely diffused in nature, but is much less abundant than sodium. It is found in many minerals and rocks, and in all good soils, since its presence is essential to the growth of plants. Formerly wood ashes were the source of potassium compounds. Large quantities of potassium chloride, and another mineral containing this salt and magnesium chloride, are mined near Stassfurth, in Germany. Potassium salts occur in small quantity in sea and spring waters.

Potassium was first isolated by Davy in 1807 by electrolysis of potassium hydroxide. Previous to this time the alkalies, sodium hydroxide and potassium hydroxide, were regarded as simple substances. Lavoisier had, however, supposed that they contained oxygen from their chemical similarity to well-known metallic oxides. The manufacture of potassium by reducing the carbonate with coal is more difficult than that of sodium, owing to the liability of the formation of a black explosive body.

Potassium is a silver-white metal, brittle at 0°, soft as wax at ordinary temperature, and melting at 62°.5. It may be distilled in an atmosphere of hydrogen at a faint-red heat. Its vapor is green.

Potassium combines with other elements more energetically than sodium. It decomposes water rapidly, and the hydrogen evolved is ignited by the intense heat of the reaction, and burns with a violet flame. The metal tarnishes immediately in ordinary air, and is soon converted into a mixture of potassium hydroxide and carbonate. It, however, does not lose its lustre in perfectly pure, dry air. Potassium is a strong reducing agent, and has been used to separate other elements from their compounds; but sodium being much cheaper, is more generally used. Sodium and potassium unite to form an alloy which is liquid at ordinary temperature and has the appearance of mercury.

Potassium Chloride, KCl, or K–Cl, crystallizes in cubes, has a stronger saline taste and is more soluble in water than sodium chloride, which it resembles in properties. It is used in the preparation of other potassium salts and in fertilizers.

Potassium Bromide, KBr, is a valuable medicine. It has a sharp saline taste, is readily soluble in water, and crystallizes in cubes.

Potassium Iodide, KI, is a very soluble salt, which forms opaque cubes when deposited from hot solutions, and transparent crystals when a dilute solution is slowly evaporated. It is much used as a medicine. Its vapor density has been found to be 84.5, theory requiring 83 for the formula KI.

Potassium Tri-iodide, KI_3, is obtained by saturating a strong solution of potassium iodide with iodine, and evaporating over sulphuric acid. It loses two atoms of iodine at $100°$.

Potassium Fluoride, KF, is a very deliquescent salt, obtained by neutralizing potassium carbonate with hydrofluoric acid. It separates in cubes when the solution is evaporated.

Hydrogen Potassium Fluoride, or Acid Potassium Fluoride, HFKF, separates in quadratic crystals, when a solution of potassium fluoride in aqueous hydrofluoric acid is evaporated. It gives off hydrofluoric acid at a dull-red heat, leaving potassium fluoride.

Rubidium, Rb.

Atomic Weight, 85.5. *Density,* 1.52.

Rubidium was discovered by Bunsen in 1861. It is widely distributed, but has been found only in minute quantities. It occurs in many spring waters, in sea water, and has been detected in plants. Metallic rubidium is obtained by the same process as that used for sodium and potassium. It is silver-white, and at − 10° is soft. It is remarkable for its low melting point, 38°.5. It oxidizes at once on exposure to air, and ignites more readily than potassium. It burns like potassium on water. The rubidium salts closely resemble the corresponding potassium salts, and the salts of the two metals crystallize in similar forms.

Rubidium Chloride, RbCl, crystallizes in cubes and is very soluble in water.

Cæsium, Cs.

Atomic Weight, 133. *Density,* 1.88.

Cæsium was discovered by Bunsen in 1860. It is a very rare element, often occurring with rubidium. It is found in some spring waters and a small number of minerals, from one of which, lepidolite, it is usually prepared. Its salts are not taken from soil by plants. Its compounds present great similarity to those of potassium and rubidium. Metallic cæsium cannot be prepared by heating the carbonate with charcoal, but it has been obtained by the electrolysis of a molten mixture of 4 parts of barium cyanide and 1 part of cæsium cyanide. The metal is soft, burns on water like potassium, and quickly ignites on exposure to air. Its melting point, 26°.5, is the lowest of any metal excepting mercury.

Cæsium Chloride, CsCl, is a salt which crystallizes in cubes and deliquesces in damp air.

SPECTRAL ANALYSIS.

THE vapors of many substances when heated so as to become self-luminous appear as bodies of characteristic colors. The necessary high temperature may in general be most conveniently secured by the electric spark, but in many cases, notably in the alkali and alkali-earth metals, the moderate temperature of the Bunsen flame is quite sufficient to cause the vapors to glow. Thus, sodium, either metallic or in combination with other non-metallic elements, will give a remarkably pure and brilliant yellow color to such a flame; while potassium, so similar in its chemical properties, will glow with a characteristic but feeble violet light. This pronounced difference in the properties of the two elements has long been known, and used as a ready guide to the process of chemical analysis of an unknown compound containing one or the other of these metals; only when both sodium and potassium are present is there any difficulty in application of the method, for then the intensity of the light due to the sodium is so great as to quite mask the feeble violet of the potassium, unless the latter substance is enormously in excess. In such a case chemists were accustomed to observe the flame through a plate of cobalt-blue glass, or a film of a solution of indigo, both of which are quite opaque to yellow, and very transparent to the peculiar light of potassium vapor. Thus a flame which to the unaided eye appears to be of a strong yellow, indistinguishable from a simple sodium flame, seen through a proper thickness of indigo solution might appear of the characteristic hue of potassium vapor.

This primitive process of qualitative analysis by the hue of a glowing vapor has undergone enormous extension of recent years, and yielded many discoveries of the greatest interest. Perfected in the hands of Bunsen and Kirchhoff, it has led

to the discovery of seven previously unsuspected elementary bodies; to the recognition of the existence of the elements familiar to our chemistry throughout the universe, so far as the stars are sufficiently bright for examination; to a solution of many of the puzzling problems of the phenomena of total solar eclipses; to a demonstration of the existence of vast cosmical bodies of luminous gases constituting true nebulæ; and to a method of determining the absolute velocity of motion of the fixed stars in the line of vision.

The fundamental principles of the modern method are as follows. If light be passed through a prism, that is, a piece of transparent material bounded by two plane polished faces, it will be deviated from a direct line towards the thicker side of the prism; consequently, since an object appears in the direction from which its light enters the eye, if one looks through such a prism at an object it will appear displaced towards the thin edge of the prism. Moreover, since the deviation produced by a prism depends upon the wave-length of the light passing through it, and a differing wave-length produces a different color sensation, the object will in general appear elongated in the direction of its displacement, and variously colored. Thus an ordinary white flame, which emits waves of all possible lengths, would appear not only displaced by a prism, but stretched out into a longer or shorter band of color—red on the end nearest the direction of the flame, violet at the farther end, and with intermediate colors similar in hue and arrangement to those of the rainbow.

If, instead of a white flame, we observe a Bunsen flame tinged by sodium vapor through the prism, we recognize a displaced image—wholly unchanged, however, as regards color : thus proving that light emitted by sodium vapor consists of only a single wave-length. Again, if a flame tinged by potassium vapor is observed through the prism, we may see two images, the less deviated being a deep red, and the more deviated a violet: whence we conclude that potassium

vapor emits two definite wave-lengths of light—one very long and one very short. If sodium and potassium are simultaneously present, we should see three images: a red—least deviated, then a yellow, and last a violet.

Such images, arranged according to the wave-lengths of light emitted by the object, are called spectra, and this method of determining the character of the light is called spectral analysis.

If the observed flame has a number of different colors, the spectral images belonging to each may overlap, and be recognized with difficulty unless the flame is a very small one. In practice a sufficiently small flame is secured by means of an
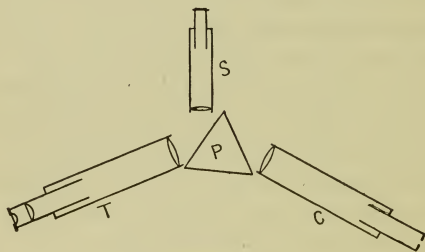
FIG. 65.

opaque screen with a narrow slit in it, the slit being parallel to the refracting edge of the prism. These two elements, the prism and the slit, are the only essential elements of the apparatus for spectral analysis, and together constitute the spectroscope. In practice, however, the spectrum is generally observed through a telescope, thus securing an increase of power which otherwise could only be obtained by a greater number of prisms. Fig. 65 represents the construction of the spectroscope as ordinarily used. Here P is the prism, T the telescope, and C a tube bearing the slit, made of adjustable width, at its end. The tube C has at its end next the prism a lens of focal length equal to its distance from the slit

—an addition which admits of the use of a much shorter tube for the slit. With this construction the tube C is called a collimator. The accessory tube S contains a photographed scale at the outer end and a lens at its focal distance from the scale at the inner. This is placed at such an angle that when the scale is illuminated it is seen by reflection from the face of the prism superimposed upon the spectrum, thus aiding in the identification of the lines of the various spectra.

Such a spectroscope, or the simpler prism-slit combination, will exhibit a single (or if powerful a closely double) yellow line as characteristic of sodium vapor, a deep red and a violet line for potassium vapor, a very brilliant red and a feeble orange line for lithium; and so on, no two elements having spectra even remotely resembling each other. Since it requires a very minute quantity of a substance to yield its characteristic spectrum, a number of rare elements have been discovered by means of the spectroscope which would otherwise have long escaped detection. Such are Cæsium, Rubidium, Thallium, Indium, Gallium, Ytterbium, and Scandium. The first four of these are named from the color of their brighter spectral lines.

Light from a white-hot solid or liquid body, when analyzed by the spectroscope, does not exhibit a system of bright lines, but an unbroken band of colors. Such a spectrum is called a continuous spectrum. If the light from the white-hot body, however, be passed through a metallic vapor and then observed by the spectroscope, a very remarkable change is recognized, provided that the vapor is at a lower temperature than the source of light. In this case the continuous spectrum is interrupted by dark lines corresponding exactly in place to the bright lines of the metallic vapor, which would be visible without the bright source of the continuous spectrum. For example, if a sodium-tinted Bunsen flame be observed by a spectroscope, a bright-yellow line will be seen; but if behind the flame a lime-light is placed, a dark line will appear in the

yellow of the continuous spectrum. The direct light of the sun exhibits thousands of such dark lines when examined by the spectroscope, one of them falling exactly in the place of the sodium line. Since this dark line is also seen double with a spectroscope sufficiently powerful to show the sodium line double, the coincidence still being perfect for each component, the conclusion that sodium vapor exists somewhere between us and the source of the white light of the sun is inevitable. In the case of iron there are several hundred dark lines in the solar spectrum, corresponding, each one, with a bright line in the iron spectrum. That the metallic vapors are in the sun itself, follows from the observed fact that neither the distance of the sun nor the thickness of the layer of air through which its light reaches us modifies the essential characteristics of the spectrum. The same conclusion follows from the similarity of the spectra of the light of the planets, since all are seen by reflected sunlight, and the generally dissimilar spectra of the fixed stars.

By a comparison of the bright-line spectra of the various elements and the solar spectrum, physicists have been able to establish the presence of the following elements in the atmosphere of the sun : Hydrogen, Iron, Sodium, Calcium, Magnesium, Titanium, Nickel.

Copper (Cuprum), Cu.

Atomic Weight, 63.3. *Density*, 8.9.

Copper was known in prehistoric times; occurring native, it was available for tools and weapons before the art of iron smelting was learned. Native copper is one of the sources of the metal in commerce, and sometimes occurs in large masses. Copper is extracted from a variety of ores, of which may be mentioned the red oxide, Cu_2O, copper pyrites, $CuFeS_2$, and

chalcocite, Cu_2S. Copper is easily separated from its salts by electrolysis, and from its oxides by heating with hydrogen or charcoal. The chemistry of the extraction of copper from its ores cannot be profitably studied without a knowledge of copper compounds.

Copper is red, tough, moderately hard, capable of a high polish, and, including its alloy, brass, ranks next to iron, the most useful of metals. It may be rolled into thin leaves and drawn into very fine wire. When hammered it becomes stiff and brittle; by heating to redness it is annealed, whether cooled quickly or slowly. Copper ranks next to silver as a conductor of heat and electricity. Its melting point is above that of silver and gold, and it is volatile at very high temperatures. Commercial copper usually contains traces of silver, arsenic, bismuth, iron, and other metals. It is, however, pure enough for most chemical purposes.

Copper is not affected by moist air free from carbon dioxide, nor by dry air, but in the ordinary atmosphere it slowly acquires a thin green coating of basic carbonate. The metal decomposes water slightly at very high temperatures. Strongly heated in air it oxidizes at once, first to red oxide and then to black oxide. In presence of air it slowly dissolves in hydrochloric and sulphuric acids and alkalies. The best solvent for the metal is nitric acid.

Copper forms two well-defined classes of compounds designated as cuprous and cupric. One atom of copper replaces one of hydrogen to form cuprous compounds; cuprous copper is, therefore, apparently a monad. The observed gas density, however, of cuprous chloride is 108, corresponding to the molecular formula Cu_2Cl_2, which requires 98.8. This shows that the double atom, Cu_2, is a dyad. In no case has the gas density of a cupric compound been observed; hence the molecular weights of cupric salts are not certainly known. One atom of copper replaces two of hydrogen in acids to form cupric salts. Copper is therefore regarded as a dyad, as, for

example, in cupric chloride, $Cu < {Cl \atop Cl.}$ In cuprous compounds
the two atoms of copper are supposed to be united by one
bond, as in cuprous chloride, Cl–Cu–Cu–Cl.

Cuprous Chloride, Cu_2Cl_2 or Cl–Cu–Cu–Cl, remains as a
brown liquid when cupric chloride is heated to redness, and
on cooling it solidifies to a brown mass. Cuprous chloride is
usually prepared by boiling a solution of cupric chloride with
metallic copper. If the solution contains much hydrochloric
acid cuprous chloride remains dissolved, while in the absence
of an excess of acid it separates as a white powder. Cuprous
chloride absorbs moisture and oxygen from the air, and is
converted into a green oxychloride. Solutions of cuprous
chloride also take up oxygen and become green; in presence
of hydrochloric acid the change may be represented as follows:

$$Cu_2Cl_2 + O + 2HCl = 2CuCl_2 + H_2O.$$

Exp. 51.—*a*. Dissolve a little copper scale in hot hydrochloric acid,
and pour the solution obtained into water. The formation of a white
precipitate of cuprous chloride is evidence that the scale contains cu-
prous oxide.

b. Place in a test-tube copper scale, copper filings or fine wire, and
hydrochloric acid, and boil the mixture gently until the green color
due to cupric chloride disappears. Cuprous chloride will separate if
but little hydrochloric is present, and the clear hot solution will deposit
more of the salt on cooling. Pour some of the solution into a porcelain
dish, and some into water. Note the changes. Formulate the reactions
between the cuprous oxide and hydrochloric acid, the cupric oxide and
the acid, and also between the cupric chloride and metallic copper.

Cuprous Bromide, Cu_2Br_2, is formed when heated copper is placed in
bromine.

Cuprous Iodide, Cu_2I_2, is formed by the direct union of copper and
iodine. Potassium iodide precipitates from a solution of cupric sulphate
cuprous iodide mixed with iodine:

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2.$$

Cupric Chloride, $CuCl_2$ or $Cu <^{Cl}_{Cl}$, is formed when copper is
burned in an excess of of dry chlorine. It is a yellowish-brown
powder, which loses half its chlorine when heated as already
mentioned. A solution of cupric chloride is best prepared by
dissolving the oxide or carbonate in hydrochloric acid. On
evaporation fine green crystals of $CuCl_2 + 2H_2O$ separate.
The concentrated solution of cupric chloride is green, and
changes to a bluish-green color on adding much water.

Exp. 52.—Dissolve cupric oxide, free from cuprous oxide, in hot con-
centrated hydrochloric acid. Dilute largely with water, and compare
the results with those obtained with cuprous chloride.

Cupric Bromide, $CuBr_2$, is obtained by dissolving cupric oxide in hydro-
bromic acid.

Cupric Iodide, CuI_2, exists in the dilute solution containing $\frac{1}{20}$ per cent
of potassium iodide, to which a 1 per cent solution of cupric sulphate
has been added. Such a solution remains clear, and does not react for
iodine with starch.

Silver (Argentum), Ag.

Atomic Weight, 107.9.   *Density*, 10.5.

Silver occurs in the free state in nature, and has been known
from the earliest times. Next to gold it has long been the
most highly prized of metals, both on account of its beauty
and valuable properties. It has been found in large masses
—one in Norway of five hundred and one in Peru of eight
hundred pounds. Native silver usually contains copper and
gold, and often mercury, platinum, antimony, and bismuth.
The larger part of the silver of commerce is obtained from
ores. Of these the most important are silver sulphide and
its combinations or mixtures with other metallic sulphides.
Galena (lead sulphide) always contains silver. Silver chloride,
bromide, and iodide are also worked as silver ores. Silver

occurs in sea water to the extent of 1 milligram in 100 liters, and has been found in the ashes of plants.

Polished silver possesses a brilliant white lustre. The surface of the metal deposited in the electro-plating process is frosted white, while finely divided silver from the reduction of silver salts by zinc or copper is gray or even black. Very thin films of silver appear blue by transmitted light. Silver ranks in malleability next to gold; it may be beaten into leaves $\frac{1}{100000}$ of an inch in thickness, and one grain may be drawn into 400 feet of wire. Silver melts at about 1000°, and may be distilled in a lime crucible by means of an oxyhydrogen flame. In contact with air molten silver absorbs 22 times its volume of oxygen gas, most of which escapes when the metal solidifies with a "spitting" or throwing out of particles of the silver. The "spitting" is prevented by covering the silver with a fusible slag to keep it from contact with the air. Silver retains its lustre in pure air; the blackening of silver ware is supposed to be due to hydrogen sulphide, which forms a thin film of black silver sulphide on the metal. Burnished silver retains its whiteness better than a surface which has been cleansed by chemicals. Silver is not attacked by dilute sulphuric acid, but dissolves in the hot strong acid. Nitric acid somewhat diluted is the best solvent for silver, dissolving it readily at ordinary temperatures.

Exp 53.—Dissolve a quarter of a dollar or other silver coin in the smallest possible quantity of nitric acid diluted with its bulk of water. The solution contains silver nitrate and cupric nitrate. Dilute with about 100 cc. of water, and place in the solution a coil of bright copper wire. The silver will precipitate on the wire as a gray spongy mass, often showing bright crystalline facets. After a time shake it from the wire, and when no more is deposited remove the wire, and wash the silver by decantation until the washings are colorless. Add some ammonia, which will dissolve a little copper adhering to the silver with formation of a blue color. Wash again until the washings are colorless. Keep the silver for future experiments.

Silver Alloys.—The alloys of silver and copper are used for coins and solid silver articles, as pure silver is too soft to withstand the wear. The copper imparts toughness and hardness, and unless present in too large proportions the alloy has the whiteness and beauty of pure silver. The United States silver coinage consists of 900 parts of silver to 100 of copper, and the British (sterling silver) contains 925 parts of silver to 75 of copper.

Silver alloys readily with many other metals, but the compounds formed are of little importance, except those of lead and zinc, which are obtained in some processes of separating silver from its ores.

Silvering and Silver Plating.—A coating of silver on other metals is highly valued because of the beauty of the silver surface and its resistance to corrosion. Copper, brass, and German silver articles may be silvered by first rubbing on a silver amalgam, heating to volatilize the mercury, and then burnishing. Or they may be rubbed with or put into a solution of a silver salt, when a thin film of silver will be deposited on them. These methods do not answer for articles which are subjected to much wear. In order to obtain a more durable coating they are electro-plated with silver. In this process the piece to be plated is placed in a solution of silver cyanide in potassium cyanide, and connected with the negative pole of a battery, and the positive pole is joined to a sheet of pure silver suspended in the solution. The galvanic current decomposes the silver cyanide, and the silver is deposited on the metallic piece as a firm, compact coating. At the same time silver passes into solution from the sheet of silver, thus maintaining the strength of the solution.

Silver may be deposited as a brilliant mirror on glass from alkaline solution to which milk-sugar or certain other organic substances have been added.

The molecular weights of silver salts are not certainly known,

as the gas density of no one of them has been observed.   One atom of silver replaces one atom of hydrogen in acids to form the common or argentic salts, and silver is therefore regarded as a monad.   The formulas of the argentic salts are consequently analogous to those of the alkali metals.   The argentous compounds are little known.

Silver Fluoride, AgF.—Silver oxide dissolves in hydrofluoric acid, and the solution yields on evaporation deliquescent crystals having the composition $AgF + 2H_2O$.

Silver Chloride, Argentic Chloride, AgCl, or Ag–Cl, is prepared by adding common salt or other soluble chloride to solutions of silver nitrate or sulphate.   The white curdy precipitate on long standing or violent agitation settles as a heavy powder, leaving the liquid clear.   When silver chloride is exposed to light it first turns violet and finally black, with loss of a little chlorine.   It is extremely insoluble in water, and but very slightly soluble in concentrated nitric acid.   One part of silver chloride dissolves in 200 parts of concentrated hydrochloric acid.   It is somewhat soluble in solutions of alkali chlorides, and is very easily dissolved by ammonia water, by alkali thiosulphates and cyanides.   Silver chloride melts at 260° to a yellow liquid, which cools to a brown, tough, and sectile mass.   If moist silver chloride is placed in contact with iron or zinc the silver gradually separates in a spongy form, and the chlorine unites with the other metal.

Silver Bromide, AgBr, is very similar in properties to silver chloride, from which it differs by being less soluble in ammonia, and having a yellow tinge as it is ordinarily precipitated.   It is used in various photographic processes.

Silver Iodide, AgI.—Silver dissolves in concentrated hydriodic acid, setting hydrogen free.   From the hot saturated solution

crystals form on cooling, which contain silver iodide and hydriodic acid. Silver iodide separates from a solution of silver nitrate on the addition of soluble iodides as a bright-yellow curdy precipitate. Pure silver iodide is changed very slowly, or not at all, by sunlight, but if mixed with silver nitrate it acquires a greenish-black color. Silver iodide resembles the chloride and bromide, but is very slightly soluble in ammonia.

Exp. 54.—Convert about half of the silver of the previous experiment into silver nitrate, $AgNO_3$, by dissolving in nitric acid. Dilute a portion of the solution largely with water, add hydrochloric acid as long as a white precipitate forms, and agitate violently until the chloride settles quickly. Wash the precipitate on a filter until free from acid. Expose a portion of the silver chloride to sunlight. Treat another part with strong ammonia water. The remainder of the silver chloride may be rinsed into a test-tube, and a piece of zinc placed in contact with it. Note the results.

Exp. 55.—Add some of the silver nitrate of the foregoing experiment to a solution of potassium bromide in a test-tube. Shake violently, and after the precipitate has subsided decant the supernatant liquid, and then add ammonia water to the precipitate. Repeat the experiment, using potassium iodide instead of potassium bromide. Formulate the reactions between the silver nitrate and the potassium bromide and iodide.

Gold (Aurum), Au.

Atomic Weight, 196.7.   *Density*, 19.3.

Gold was prized in prehistoric times for its beauty, its durability, and ease of working. It usually occurs in the free state, sometimes crystallized in octahedral and dodecahedral forms, but usually in irregular nuggets, flattened scales, or "fine dust." It is widely distributed, though found in comparatively few localities in paying quantities. Most river sands contain gold. Traces of gold are found in copper and iron pyrites, galena, and in many silver ores, and a very

minute proportion occurs in sea water. Native gold always contains silver, and sometimes minute quantities of copper, iron, palladium, and rhodium.

Pure gold in mass has a bright-yellow color, is somewhat harder than lead, and is the most malleable and ductile of metals. Gold-leaf may be beaten out so thin that 280,000 leaves together have but an inch of thickness, and one grain of gold has been drawn into a wire 500 feet long. The thinnest gold-leaf and a thin deposit of gold upon glass appear green by transmitted light. Finely divided gold suspended in a liquid has a red color by reflected and a blue color by transmitted light.

Gold melts at about 1240°, and at the highest temperature of a wind-furnace it volatilizes slightly. Gold does not oxidize or tarnish in the air at any temperature, and is not altered by sulphur, which blackens silver. It is not acted upon by any single acid, excepting selenic, under ordinary circumstances. When, however, gold immersed in sulphuric acid is made the positive electrode of a galvanic battery, it dissolves, and in nitric acid under like conditions a violet precipitate forms. Finely divided gold dissolves when heated with concentrated sulphuric acid, mixed with either iodic acid, potassium permanganate, or manganese dioxide.

The ordinary solvent for gold is a mixture of hydrochloric and nitric acids. Solutions containing free chlorine or bromine attack it ; iodine has slight action.

Gold Alloys.—Gold mixes in fusion with most metals, but its important alloys are those with silver and copper. These alloys are harder and more useful than pure gold. The proportion of gold in jewelry is expressed in carats, 24 carats being pure gold, and the fineness of bullion is represented in parts per thousand. United States gold coin is 900 fine or 21.6 carats, and British coin is 916.66 or 22 carats, fine. The alloys of gold and silver have a lighter color than pure gold, and with certain

proportions of silver are of a greenish-yellow color. Copper imparts a reddish tinge. The alloys used for jewelry contain both copper and silver, in varying proportions according to the color desired ; 14-carat gold possesses good color, and is well adapted for watch-cases and trinkets.

Refining.—"Fine gold" is obtained from bullion and alloys by "parting," i.e., dissolving out the base metal with hot nitric acid or sulphuric acid. If more than 25 per cent of gold be present, the alloy is melted with sufficient silver to reduce the gold to that proportion, as richer alloys do not leave pure gold when treated with acids.

Exp. 56.—*a.* Alloy, by melting together on charcoal, a gold dollar with 3 parts pure silver, or silver coin. Hammer or roll out the button into a thin strip, annealing from time to time by heating to dull redness. Roll the strip into a compact coil, and boil it with nitric acid of density 1.30. After the action has ceased decant off the acid solution, and boil with a fresh portion of acid. Wash by decantation, adding the first washings to the nitric acid solutions, from which the silver may be recovered by precipitation as chloride. See Exp. 54.

b. Take about one fourth of the gold, dry, and fuse it on charcoal with the blowpipe. Hammer out the globule of fine gold somewhat, and anneal.

c. Dissolve the remainder of the gold in a mixture of 3 parts of concentrated hydrochloric and 1 part of nitric acid. The solution contains hydrogen auric chloride, $HAuCl_4$. Evaporate the solution nearly to dryness, add 100 cc. of water, and reserve for further experiment.

Gold is also refined by the following method :

The alloy—coin for example—is fused under borax, and a stream of chlorine gas is passed into the molten metal. The metals, other than gold, are converted into chlorides, which may be poured off as soon as the gold cools and solidifies.

None of these refining processes yield entirely pure metal, and, in order to remove the last traces of silver, the gold is dissolved in nitrohydrochloric acid, and precipitated from the solution by oxalic acid or ferrous sulphate.

Exp. 57.—*a*. Take 10 cc. of gold solution, add a small crystal of oxalic acid, then potassium carbonate till the solution becomes clear, then an excess of oxalic acid, and boil; the gold quickly separates in yellow spangles.

b. Dissolve a bit of ferrous sulphate, half the size of a pea, in half a test-tube of cold water. Add two or three drops of gold solution to half a test-tube of water, and mix the two liquids. The gold will be precipitated in so fine a state as to remain suspended in the liquid, and will appear red by transmitted light and bluish by reflected light.

Amalgam.—Gold unites readily with mercury, and apparently dissolves in an excess of the latter metal, but on straining the mixture through wet leather a solid amalgam is obtained, and the strained mercury contains only a trace of gold. A very small quantity of mercury is sufficient to whiten the surface of gold.

Gilding.—Gold-leaf is used for gilding wood, paper, and leather, being made to adhere by means of glue or varnish. Metals were formerly gilded by rubbing with a gold amalgam, the mercury being then expelled by heat, or they were dipped into a solution of gold; but these methods are largely replaced by the electro-plating process. The amount of gold required to cover a metallic surface is exceedingly small. China and glass are gilded by applying precipitated gold (*Exp.* 57, *b*), with oil of turpentine, fusing upon the surface of the ware, and burnishing.

Gold Purple.—A solution of stannous chloride containing a little stannic chloride produces in solutions of gold chloride a purple-red precipitate which sometimes inclines to violet or brownish red, and has long been known as Purple of Cassius. This precipitate is insoluble in hydrochloric acid. Its composition is doubtful, and in the moist state it does not appear to contain metallic gold, as it is soluble in ammonia. It does not give off oxygen on heating, a fact due perhaps to the

stannous compounds in it taking up any oxygen separated by heat from the gold.

A gold purple is also obtained by adding an excess of magnesia to a solution of gold chloride. In this case the gold is precipitated as hydroxide on the magnesia. The magnesium chloride formed is removed by washing with water, and the mixture of gold hydroxide and magnesia is ignited. The color of the product varies with the proportion of gold present; 0.1 per cent producing a faint tint, and 5 per cent a fine purple. In place of magnesia the gold may be precipitated on other substances, and a similar purple obtained. The color appears to be due to finely divided gold which reflects red light. Gold purple is used to give a fine red color to glass and porcelain.

Exp. 58.—Boil a piece of tin foil with hydrochloric acid until it is mostly dissolved, pour off the solution of stannous chloride, and add to it a drop or two of chlorine water to convert some of the stannous chloride into stannic chloride. Finally, mix with a dilute solution of gold.

Aurous Chloride, AuCl, is prepared by heating chlorauric acid or auric chloride to 185°. It is a yellowish powder, which, in contact with water, decomposes into gold and auric chloride :

$$3AuCl = 2Au + AuCl_3.$$

Gold Dichloride, Auroso-Auric Chloride, $AuCl_2$ or Au_2Cl_4, is prepared by acting on spongy gold with dry chlorine gas. It is a dark-red hygroscopic substance. It decomposes in presence of water into aurous and auric chlorides, which may be separated by quick filtration. The aurous chloride by prolonged action of water is further resolved into gold and the trichloride.

Auric Chloride, $AuCl_3$.—Gold trichloride is formed when chlorine is passed over gold-leaf heated to 220–230°. It may

be sublimed in a stream of chlorine and obtained in reddish crystals. A solution of $AuCl_3$ is prepared by acting on gold dichloride with water, when metallic gold is separated and $AuCl_3$ is formed. The solution of auric chloride is brownish red, and yields on evaporation orange-red crystals of $AuCl_3 + 2H_2O$.

Chlorauric Acid, Hydrogen Auric Chloride, $HAuCl_4$ or $HCl.AuCl_3$.—This substance is known only in combination with water. On adding hydrochloric acid to a solution of auric chloride the color changes from red to yellow, and the solution yields on evaporation yellow crystals of $HAuCl_4 + 4H_2O$. The same compound is commonly made by dissolving gold in aqua regia (Exp. 56, c). The crystals are deliquescent, and on moderate heating lose hydrochloric acid, chlorine, and water, and are converted into aurous chloride, which on heating more strongly is resolved into metallic gold and chlorine.

Chlorauric acid forms a number of salts, as for instance sodium chloraurate, $NaAuCl_4 + 2H_2O$. This salt is obtained in crystals by adding NaCl to a solution of $HAuCl_4$ and evaporating the solution.

THE SIXTH GROUP.

THE members of this group are oxygen, sulphur, selenium, tellurium, chromium, molybdenum, and uranium.

Oxygen, O.

Atomic Weight, 16.   *Molecule*, O_2.

Oxygen is a colorless, tasteless, and odorless gas. It occurs in the free state in the atmosphere, which is a mixture of about one fifth oxygen and four fifths nitrogen by volume. It is distinguished from all other gases, nitrous oxide excepted, by causing a glowing splinter of wood to inflame. It is the supporter of ordinary combustion, and substances which burn in air burn with increased brilliancy in oxygen.

Oxygen was first isolated from other gases by Priestley in the year 1774, who obtained it from red oxide of mercury. He discovered that when this substance is heated a gas is given off which is insoluble in water, and supports combustion better than air. Previous to 1774 the air was regarded as a mixture of two gases, one of which supports combustion.

Oxygen is the most widely distributed and abundant element of the earth's crust. It constitutes nearly one half of the weight of most rocks and soils, eight ninths of water, and a large proportion of the weight of animals and plants.

Oxygen gas has a density of 16 (hydrogen as unity), and is about one tenth heavier than atmospheric air. It liquefies at $-118°$ at a pressure of 50 atmospheres, and boils at $-181°$ under a pressure of one atmosphere. The density of liquid

oxygen is 1.124. Oxygen is very slightly soluble in water, 100 volumes absorbing at ordinary temperature about 3 volumes of the gas.

Oxygen is obtained by heating various compounds of it and by the electrolysis of water. Potassium chlorate is commonly used in the laboratory in preparing oxygen. The salt, when heated, is decomposed into potassium chloride and oxygen :

$$KClO_3 = + KCl + 3O.$$
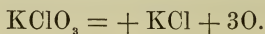
The reaction occurs at lower temperatures, and the evolution of gas is more regular if the chlorate is mixed with half its
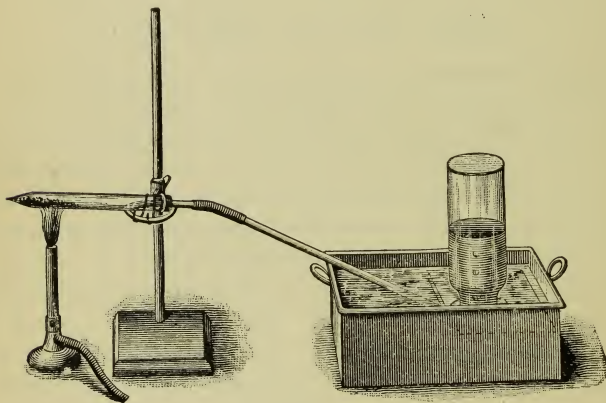
FIG. 66.

weight of manganese dioxide. The action of the dioxide is not understood. It does not give off oxygen at the temperature required to decompose the chlorate of the mixture, and remains unchanged mixed with potassium chloride after the heating.

Exp. 59.—Heat a little red mercury oxide, HgO, in a narrow hard-glass tube closed at one end. Place a glowing splinter in the escaping

gas. Represent by an equation the decomposition of the mercury oxide.

Exp. 60.—Mix 10 grams of potassium chlorate in crystals with half, or better an equal weight of manganese dioxide, and place the mixture in an ignition-tube about the size of, but a little heavier than, a common test-tube. Connect the ignition-tube by means of a cork with delivery-tube having a joint of rubber tubing. Fasten the ignition-tube with copper wire to a lamp-stand ring, as shown in Fig. 66, so that the end with the cork shall be a little lower than the sealed end. Heat cautiously with a lamp held in the hand, and collect the gas over water. When the evolution of gas ceases, remove the delivery-tube from the water. Jars containing oxygen may be taken from the water-pan by closing them with wet cardboard, and left covered with the cardboard until required for use. But little gas will escape in half an hour. Oxygen thus prepared will show a slight cloud, and will contain a little chlorine. The former will disappear, and the latter will be absorbed by water after a time.

Calculate the weight and number of liters of oxygen which 10 grams of potassium chlorate will yield. The weight of one liter of oxygen at 0° and 760 mm. may be found by multiplying the weight of 1 liter of hydrogen by the density of oxygen.

Exp. 61.—Thrust a glowing splinter of wood into a jar of oxygen.

Exp. 62.—Place a piece of charcoal on a chalk spoon, which is supported by a copper wire passing through a cardboard cover. Ignite a corner of the charcoal and place it in a jar of oxygen, as shown in Fig. 67.

Exp 63.—Anneal a thin watch-spring by heating to redness in the lamp flame, and bend it into a spiral. Fasten one end into a cardboard cover and stick the other end into a piece of match-stick about $\frac{1}{8}$ of an inch long. Ignite the bit of wood, and when it is partly burned place the watch-spring in a pint jar of oxygen. The burning wood serves to heat the iron to the temperature at which it burns in oxygen.

Fig. 67.

Exp. 64.—Place a bit of sulphur on a chalk spoon in oxygen. Note whether any changes occur. Ignite the sulphur and put again into oxygen. Notice odor, and test the gas in the jar after the combustion with blue litmus paper.

Exp. 65.—Burn a small bit of phosphorus in oxygen, and test the water in the jar with blue litmus paper. This experiment should not
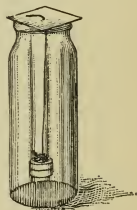
be attempted by beginners on account of liability to severe burns in handling phosphorus.

Exp. 66.—Lift from water a half-gallon jar of hydrogen, and, holding the jar mouth downwards, ignite the gas; then pass a tube from which a slow stream of oxygen is issuing into the hydrogen. The tube should be tipped with a smaller tube of platinum foil.

Exp. 67.—*a.* Heat a piece of platinum wire in a hydrogen flame from a compound blowpipe, then turn on oxygen and observe that the flame becomes smaller and that the platinum melts.

The quantity of heat produced by burning a given amount of hydrogen is the same whether the gas burns in air or pure oxygen. When, however, it burns in air the flame is largely diluted with and cooled by the nitrogen of the air, the nitrogen taking no part in the combustion.

b. Heat a piece of chalk in the compound blowpipe flame. The light thus obtained is known as the calcium light, and is used when a very intense light is required. In place of hydrogen, illuminating gas is commonly employed for the calcium light.

c. Melt the end of a file and volatilize a bit of zinc with the compound blowpipe flame. The zinc is supported on a piece of charcoal.

The burning of fuels, illuminating oil and gas is a rapid chemical union of the carbon and hydrogen in them with the oxygen of the air, carbon dioxide gas and water being formed. Oxygen is commonly called the supporter of combustion, but fuel is as truly a supporter of combustion, since it is essential to a fire, and in this sense oxygen may be regarded as a fuel. In Exp. 66 we have seen that hydrogen is apparently the supporter of the combustion of a jet of oxygen.

The combining of oxygen with substances is termed oxidation, and the compounds thus formed are called *oxides*. Many bodies slowly unite with oxygen, especially in moist air. Iron, for example, rusts, taking both oxygen and water from the air. Oxidation goes on gradually in the decay of animal and vegetable substances. All of the elements, excepting fluorine, are known to unite either directly or indirectly with oxygen.

Ozone : Molecule, O_3.—When an electric discharge passes through oxygen a peculiar odor is noticed, and the gas pos-

sesses more active properties, a portion of the oxygen having changed to an allotropic* modification known as ozone.

Under favorable conditions but a few per cent of a given volume of oxygen can be ozonized, but by passing oxygen containing ozone through a tube cooled to $-181°$ by means of liquid oxygen, pure ozone may be obtained as a steel-blue liquid, boiling at $-106°$ and changing to a blue gas. The gas density of ozone has been found to be 24; its molecular weight is therefore 48. Ozone gradually reverts to oxygen at ordinary temperature, and quickly at $200°$.

Ozone is produced in minute quantities in many cases of combustion, and in the electrolysis of water. It differs from ordinary oxygen in that it is more active chemically. Silver and mercury, which are not affected by ordinary oxygen, are at once oxidized by ozone not perfectly free from water.† Ozone liberates iodine from potassium iodide, and rapidly oxidizes many animal and plant substances. Air containing rather more than sufficient ozone to be perceptible by the smell, has an irritating effect on the throat. The atmosphere contains ozone, but the quantity is so small that it is detected with difficulty.

Exp. 68.—The tube AB, Fig. 68, contains a platinum wire, sealed into the end A. About the tube is a coil of copper or platinum wire. The wash-bottle C contains concentrated sulphuric acid to dry the oxygen which is supplied from a gas-holder. Pass a slow current of oxygen through the apparatus and into the jar D, in which is hung a strip of paper smeared with starch-paste containing potassium iodide. The test-paper will not change color. Connect the inner and outer wires of the tube with an induction coil giving a half-inch spark. A silent dis-

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* *Allotropy* is the property of existing in two or more modifications, differing in physical or chemical properties, or both. Thus there are the ordinary and ozone forms of oxygen, and the three forms or modifications of carbon, namely, charcoal, graphite, and diamond.

† Shenstone and Cundall have found that ozone, dried by long exposure to phosphorous pentoxide, reverts to oxygen after contact for some hours with mercury, without apparently oxidizing the metal.

charge of electricity will take place between the inner surface of the tube and the platinum wire, and the odor of ozone will soon be perceptible. The test paper will be colored blue by the liberated iodine. The reaction between the ozone, potassium iodide and water is as follows:

$$O_3 + 2KI + H_2O = 2KOH + I_2 + O_2.$$
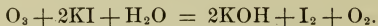
Other substances, chlorine for example, liberate iodine from potassium iodide, but in the change potassium salts are formed which are not alkaline towards litmus paper. Hence, to show the presence of potassium hydroxide, KOH, as indicated by the equation, expose to ozone a delicate red litmus paper, and one which is saturated with a dilute solution of potassium iodide. The former will not change color, showing the absence of an alkaline gas; while the paper with the iodide
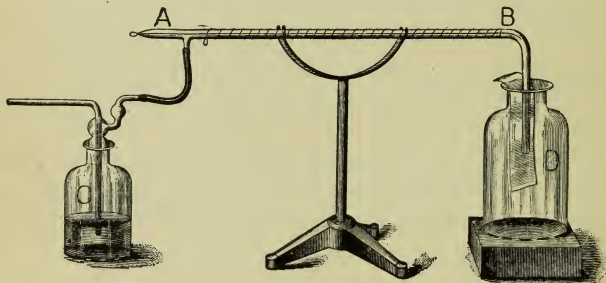
Fig. 68.

will be colored blue by the potassium hydroxide formed. A similar test-paper exposed to chlorine will not turn blue.

Exp. 69.—Agitate some clean dry mercury in a jar of dry oxygen. It will not change in appearance. Next shake up some mercury in a jar of ozonized oxygen. The metal will lose its clean, bright surface, and will stick to the glass. After a few minutes the gas in the jar will not react for ozone with potassium iodide starch-paper.

Exp. 70.—Connect the end of the ozonizing tube (Fig. 68) by means of a black rubber tube with a glass tube, and attempt to collect the gas over water. In a few minutes the rubber will be perforated by the ozone.

Exp. 71.—Place some pieces of phosphorus in a large jar of air, and partly cover them with water to prevent the phosphorus from inflaming. After a time test the air in the jar for ozone.

Exp. 72.—Hang a wet potassium iodide starch paper in a pint jar containing a few drops of ether, and introduce a hot glass rod. The ether will be oxidized to a pungent body known as aldehyde, and at the same time a portion of the oxygen of the air in the jar will be ozonized.

Hydrogen and oxygen unite to form the compounds hydrogen monoxide or water, H_2O, and hydrogen dioxide, H_2O_2.

Water, H_2O or H–O–H.—The abundance of water is familiar to all. It forms a large proportion of the weight of animals and plants, and is a constituent of many minerals and salts, and is always present in the atmosphere.

Water is a tasteless, odorless liquid, boiling at 100° under a pressure of 760 mm. of mercury. It may be cooled below 0° without freezing, but the temperature of melting ice is practically constant, and is not changed to a measurable extent by the ordinary changes in atmospheric pressure. Water and ice give off vapor when exposed to the air. The following table gives the pressure of the vapor of water at different temperatures :

TABLE OF THE PRESSURE OF THE VAPOR OF WATER.

Temperature.	Pressure in millimeters of mercury.	Temperature.	Pressure in millimeters of mercury.	Temperature.	Pressure in millimeters of mercury.	Temperature.	Pressure in Atmospheres. 1 atmosphere = 760 mm. of mercury.
— 20°	0.927	12	10.457	25	23.550	100	1
0	4.600	13	11.162	26	24.988	111.7	1.5
1	4.940	14	11.908	27	26.505	120.6	2
2	5.302	15	12.699	28	28.101	127.8	2.5
3	5.687	16	13.536	29	29.782	133.9	3
4	6.097	17	14.421	30	31.548	144.0	4
5	6.534	18	15.357	40	54.906	159.2	6
6	6.998	19	16.346	50	91.982	170.8	8
7	7.492	20	17.391	60	148.791	180.3	10
8	8.017	21	18.495	70	233.093	224.7	25
9	8.574	22	19.659	80	354.280	....	....
10	9.165	23	20.888	90	525.450	....	....
11	9.792	24	22.184	100	760.	....	....

Exp. 73.—The boiling of water at less than atmospheric pressure may be shown by an apparatus such as represented by Fig. 69. The vessel *A* has a capacity of about a liter. Its neck is surrounded by the tube *D*, through which water may be passed. The thermometer should not touch the sides of the neck of *A*. The tube *B* has a diameter of 8 to 10 mm., and a height above *C* of 800 mm.

Boil water vigorously in *A* until the air is expelled, allowing the steam to escape freely from the lower end of *B*, and then place a vessel containing mercury under *B* as indicated by the figure, and remove the lamp used in heating the water. To avoid danger in case *A* should crack, it is surrounded by a glass jar with card-board cover, as shown. The water will continue to boil, and the mercury will rise in *B*. On passing a stream of water into the jacket-tube *D*, the steam will be rapidly condensed, and the water will boil intermittingly until the thermometer has fallen to about 30°, when the column of mercury in *B* will be found to be about 30 mm. shorter than the barometric column.
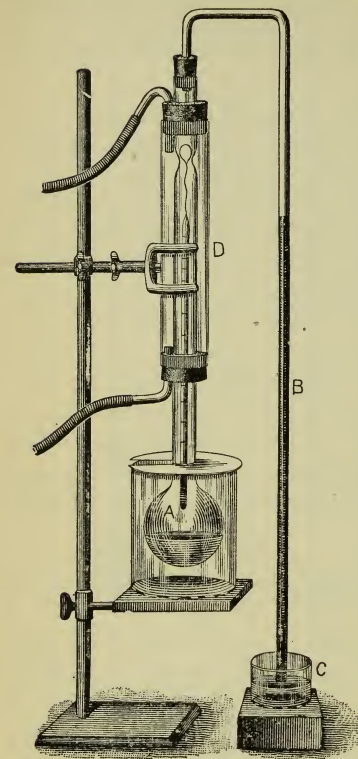
Fig. 69.

Pure water has a bluish-green color when viewed in large mass. It has the maximum density at 4°, and it expands slightly when the temperature sinks below or rises above this point. Water in freezing increases in volume nearly $\frac{1}{11}$, hence ice always floats on water.

Water is the most common solvent, dissolving very many salts and other bodies and gases. Solution is a physical phenomenon, accompanied in some cases by chemical changes. Common salt dissolves unchanged, and may be recovered by evaporating the water. Sodium also dissolves in water, part of which is decomposed, and the solution yields on evaporation not sodium, but sodium hydroxide.

Rain water is nearly pure, but river and spring waters contain saline matter dissolved out of the soil and rocks through which the water has passed. Vegetable matter and products of its decay are often serious impurities in drinking water. Some spring waters owe their medicinal properties to the salts they contain, or to the gases hydrogen sulphide and carbon dioxide held in solution. Sea water contains about 3.5 per cent of solid matter—mostly common salt. For ordinary laboratory uses water is purified by distilling and condensing the steam in a block-tin pipe. Glass does not answer well, as it is slightly soluble in water.

Exp. 74 —Boil tap water in a glass retort, and condense the steam in a flask placed over the neck of the retort. The flask may be placed in a pan containing water, and cooled by turning occasionally, or covering with a wet towel. Notice when heating the water in the retort that air bubbles escape before the water boils, and that the steam which fills the retort when the water is boiling is invisible. After about two thirds has distilled, evaporate a few drops of the distilled water on platinum foil. A faint residue will be perceptible on heating the foil to redness. Evaporate as before some of the water remaining in the retort.

Composition of Water.—Numerous experiments have been made with the greatest possible care in order to find the proportion of oxygen which is contained in water. The weight of evidence thus far obtained indicates that 15.96 weights of oxygen combine with 2 weights of hydrogen, and that the atomic weight of oxygen is a little less than 16, the number adopted in this book.

Two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam :

| 1 | 1 | $+$ | 16 | $=$ | 9 | 9 |

Hydrogen.   Oxygen.   Steam.
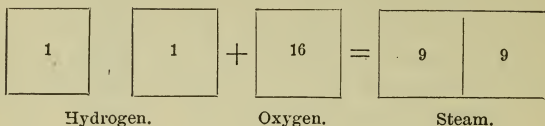
The gas density of steam is 9; twice the density equals 18, the molecular weight of water. In 18 weights of water are 2 weights of hydrogen, the weight of 2 atoms of hydrogen; and 16 weights of oxygen, the weight of 1 atom of oxygen. The water molecule is, therefore, composed of 2 atoms of hydrogen and 1 atom of oxygen, and has the formula H_2O. The reaction occurring when the gases unite has commonly been represented thus :

$$2H_2 + O_2 = 2H_2O.$$
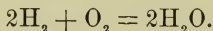
Later it will be shown that the change is probably more complicated.

The burning of hydrogen with pure oxygen produces the intense heat of the compound blowpipe, which Bunsen has calculated to be 2844°. The quantity of heat evolved is very large, 2 grams of hydrogen burned with oxygen producing 68,360 calories.

Exp. 75.—Blow a small soap-bubble with a mixture of 2 volumes of hydrogen and 1 volume of oxygen contained in a rubber gas-bag. Remove the bag and apply a flame to the bubble. The shock is due to the expansion caused by the intense heat of the combustion, and also to the sudden condensation of the steam formed, producing a partial vacuum into which the air rushes. There is danger of injuring the ears if the large quantities of the mixed gases are exploded.

Exp. 76.—Remove the flask *F*, Fig. 70, and ignite a jet of oxygen and hydrogen at the blowpipe-tip *A*, then turn the flame low and replace

the flask. As soon as the moisture is driven from the upper part of it the flame may be made larger. The steam formed will be condensed in the cooling-tube C. When a little water has been collected in the beaker, the latter may be held up against the delivery-tube, so that escaping gas shall bubble through the water; then the supply of oxygen may be regulated so that little or no gas escapes. The height of the water in the gas-holders supplying oxygen and hydrogen should now be marked, and again at the close of the experiment. In case the flame is accidentally extinguished, the gas in the flask F should be displaced by a current of air, to make sure before relighting that F does not contain an explosive mixture of oxygen and hydrogen.

Exp. 77.—Pass a current of electricity from 4 or 6 Bunsen cells through water containing $\frac{1}{10}$ by volume of sulphuric acid. The apparatus represented by Fig. 71 is convenient for this purpose. The hydrogen obtained may be tested by burning it,

FIG. 70.

and the oxygen by holding a glowing splinter in the escaping gas when the stopcock is opened. If the two gases are measured very accu-

FIG. 71.

rately it will be found that for every two volumes of hydrogen collected there is slightly less than 1 volume of oxygen, as the latter is more soluble in water than the former, and a very small part of the oxygen exists as ozone, as may be proved with a potassium iodide starch test-paper. Pure water is a poor conductor of electricity, and is not decomposed by it. It is supposed that the sulphuric acid in the solution electrolyzed is first decomposed into hydrogen, oxygen, and SO_3, thus:

$$H_2SO_4 = H_2 + O + SO_3.$$
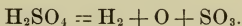
SO_3 is known to form sulphuric acid with water : $SO_3 + H_2O = H_2SO_4$. Whatever may be the changes, the quantity of sulphuric acid in the solution is not diminished by the electrolysis.

The best method of obtaining a mixture of 2 volumes of hydrogen and
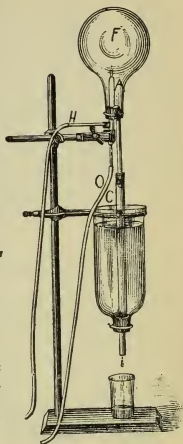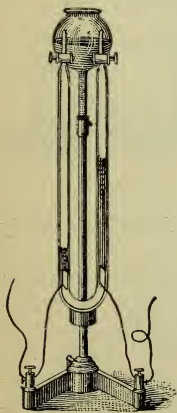
1 volume of oxygen is to decompose dilute sulphuric acid by electricity
in the apparatus shown in Fig. 72. The air in the apparatus is expelled
by the escaping gases, and the quantity of ozone formed is too small to
interfere with most uses of the mixed gases.

Exp. 78.—The apparatus represented by Fig. 73 is designed to show
the volume of the steam which results from the union of known vol-
umes of hydrogen and oxygen. The tube A is of stout glass, 80 or 90
cm. in length, and having a diameter of about 12 mm. Two platinum
wires are sealed into the upper and closed end. These ends within the
tube are near together, but not in contact. The tube A is heated by
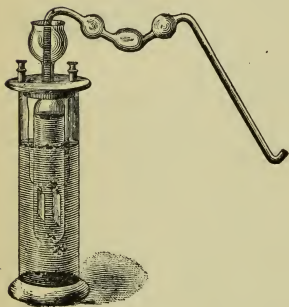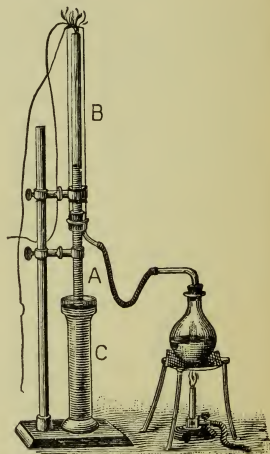
FIG. 72.   FIG. 73.

steam passed into the jacket-tube B. The glass cylinder C is nearly
filled with mercury.

Dry A thoroughly by warming and sucking air through it by means
of a long glass tube, and while still warm fill it with warm clean mer-
cury. Adhering bubbles of air may be removed by allowing a large bub-
ble to pass the length of the tube several times. When A is filled with
mercury close it with the thumb, and place the open end under the mer-
cury in the cylinder. Pass steam into the jacket-tube, and allow a mix-
ture of two volumes of hydrogen and one of oxygen from the apparatus
shown in Fig. 72 to bubble into A. Mark the volume of the gas by

means of a strip of paper pasted on B, and also mark the height of the mercury in A above the mercury in C. A strip of wood cut the length of the mercury column is a convenient measure. Next lower A together with B until the end of A rests on a rubber pad in the bottom of the cylinder, and pass a spark from an induction coil between the wires sealed in A. The feeble flash followed by a contraction of the gas indicates that combination has occurred. Finally, raise A until the mercury in it stands at the same height as before the explosion. The steam in A is now under the same pressure and at the same temperature as the mixed gases, and occupies two thirds the volume of the mixed gases taken.

Hydrogen Dioxide, H_2O_2, or H–O–O–H, is obtained by the slow evaporation of its aqueous solution as a colorless liquid, having a density of 1.45. It is soluble in all proportions in water, and is readily soluble in ether. The concentrated aqueous solution gives off oxygen slowly at 20° and with explosive violence at 100°, hydrogen dioxide decomposing into water and oxygen:

$$H_2O_2 = H_2O + O.$$
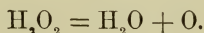
Dilute solutions are more stable, and when distilled a small portion of hydrogen dioxide passes over with the steam.

Hydrogen dioxide acts as a bleaching agent, though not as rapidly as chlorine. It is found useful in restoring oil paintings which have been blackened by lead sulphide, and has been used in medicine. It serves as a reagent in qualitative analysis, and for the preparation of a number of compounds. Hydrogen dioxide is a strong oxidizing agent, readily giving up half its oxygen to many bodies, and is remarkable for its reaction with certain metallic oxides, which are reduced by it to the metallic state. Thus if silver oxide, Ag_2O, is placed in a dilute aqueous solution of hydrogen dioxide, oxygen gas will escape, and finely divided metallic silver will remain:

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$
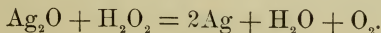
Ozone in contact with a solution of hydrogen dioxide is changed to ordinary oxygen, thus :

$$O_3 + H_2O_2 = H_2O + 2O_2.$$
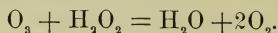
Hydrogen dioxide sets free iodine from metallic iodides, and the following reactions are employed in testing for the presence of it in solutions :

$$\underset{\text{Potassium iodide}}{2KI} \quad + \quad H_2O_2 = \underset{\text{Potassium hydroxide}}{2KOH} \quad + I_2.$$

$$\underset{\text{Ferrous iodide}}{2FeI_2} \quad + \quad 3H_2O_2 = \underset{\text{Ferric hydroxide}}{2Fe(OH)_3} + 2I_2.$$
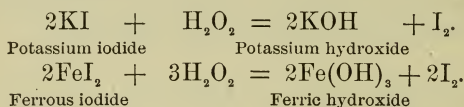
The first reaction takes place very slowly in highly dilute solutions, and immediately in concentrated solutions. But little iodine will remain in the free state, as the potassium hydroxide will combine with it. The solution, however, will react alkaline, and also for iodine with starch. Ferrous iodide is decomposed immediately by very dilute solutions of hydrogen dioxide.

Compounds containing the group OH are called hydroxides, and to OH the name Hydroxyl has been given. Hydrogen dioxide is free hydroxyl. Its molecular weight has not been determined, but the molecule H_2O_2 is assumed because of its decomposition into water and oxygen.

Water formed by synthesis, as in Exp. 76, does not contain a trace of hydrogen dioxide. But when a hydrogen flame impinges on water for a short time hydrogen dioxide may easily be detected, making evident the formation of it in the union of hydrogen and oxygen in the presence of water. The simplest view of the reaction is that a molecule of hydrogen, H_2, unites with a molecule of oxygen, O_2, to form H_2O_2.

If it is true that hydrogen dioxide is the first product of the combustion of hydrogen with oxygen, then the formation of water may be due to the decomposition of hydrogen dioxide by heat, thus :

$$H_2O_2 = H_2O + O.$$

The free atom of oxygen may unite directly with a hydrogen molecule to form another water molecule :

$$H_2 + O = H_2O.$$
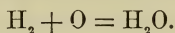
Or the free oxygen atom may unite with another free oxygen atom to form O_2.

Traube, who discovered this synthesis of hydrogen dioxide, suggests that the reaction may be as follows :

$$H_2O + O_2 = 2H_2O + H_2O_2.$$

(1) $H_2 + H_2O$

(2) $H_2O_2 + H_2 = 2H_2O.$
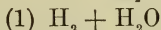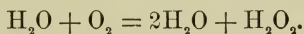
The second equation represents the formation of water by the reducing action of hydrogen on hydrogen dioxide. That the formation of hydrogen dioxide is not due to the addition of oxygen to the water molecule is supported by the fact that the most powerful oxidizing agents are without action on water.

It is possible that the presence of water is essential to the combination of hydrogen and oxygen in the same way that it is in the reaction between carbon monoxide and oxygen, which will be considered later. The absence of hydrogen dioxide in the ordinary synthesis of water is owing to its instability at high temperatures. When hydrogen burns on the surface of water some of the hydrogen dioxide dissolves in the cool water, and is thus removed from the action of heat. In the combustion of carbon monoxide and also of illuminating gas on the surface of water hydrogen dioxide is formed.

Hydrogen dioxide is commonly prepared by acting on barium dioxide, BaO_2, with a dilute acid:

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$
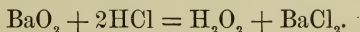
The barium chloride, $BaCl_2$, is a soluble salt, and remains

in solution. When sulphuric acid is used, barium sulphate, $BaSO_4$, is precipitated, and may be removed by filtration:

$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4.$$
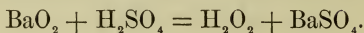
The dilute solution may be concentrated by evaporation in vacuum over sulphuric acid. The presence of a little free acid renders it less liable to decompose.

Exp. 79.—Dilute hydrochloric in a test-tube with three or four times its bulk of water, and add gradually barium dioxide until it ceases to dissolve readily. The cheap barium dioxide of commerce will answer, although it is too impure for the preparation of concentrated solutions. Add to a small portion of the solution a few drops of thin starch paste containing a little potassium iodide.

It has already been shown that other substances (what ?) set free iodine from potassium iodide; hence the reaction is not characteristic for hydrogen peroxide.

Exp. 80.—Dilute a portion of the hydrogen dioxide solution until no coloration appears on adding starch-paste and potassium iodide. Then add one drop of a dilute solution of ferrous sulphate or a minute fragment of the salt to the solution. The blue color will be seen at once. The ferrous sulphate, $FeSO_4$, and potassium iodide react with formation of ferrous iodide and potassium sulphate, thus :

$$FeSO_4 + 2KI = FeI_2 + K_2SO_4.$$
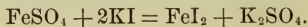
As already stated, hydrogen dioxide sets free iodine from ferrous iodide. An excess of ferrous sulphate interferes with the reaction. Dilute solutions of hydrogen dioxide containing starch and potassium iodide become blue on standing some time.

Exp. 81.—Hold a small jet of hydrogen burning at the end of a glass tube 3 or 4 mm. wide on the surface of water in a small porcelain dish. After some minutes test the water for hydrogen dioxide. The hydrogen for this experiment is best obtained from dilute sulphuric acid and zinc. That from impure hydrochloric acid does not answer. For the three following tests the dilute solution of hydrogen peroxide furnished by druggists answers.

Exp. 82.—To a solution of hydrogen peroxide, which should be nearly neutral, add a solution of pure potassium iodide. Free iodine will be

evident from the red color, and the solution will react alkaline to delicate red litmus paper, owing to the presence of potassium hydroxide.

Exp. 83.—Place a test-tube containing not too dilute a solution of hydrogen dioxide in hot water; oxygen gas will escape.

Exp. 84.—Add silver oxide to a solution of hydrogen dioxide. If the solution is not too dilute, sufficient oxygen may be obtained to test.

The Oxides and Hydroxides of the Seventh Group.*

Chlorine Monoxide, Hypochlorous Oxide, Cl_2O or $Cl-O-Cl$, is a yellowish-colored gas with a penetrating odor, resembling that of chlorine. Its observed gas density corresponds to that required by the formula Cl_2O. It condenses to a liquid, boiling at about $-19°$, which explodes violently when poured from one vessel to another, or when heated. Chlorine monoxide is prepared by passing dry chlorine over dry mercuric oxide, which reacts with formation of mercuric chloride and hypochlorous oxide :

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$
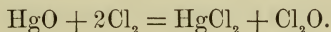
Hypochlorous Acid, $HClO$ or $Cl-OH$, is known only in dilute aqueous solution. It is formed when hypochlorous oxide is dissolved in water. It is prepared by adding precipitated mercuric oxide to chlorine water:

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2ClOH.$$
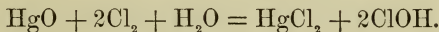
On distillation the dilute acid passes over, and mercuric chloride remains. Hypochlorous acid can also be obtained from its salts. It is a powerful bleaching agent, yielding its

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* It is better to become familiar with the theory of acids, bases, and salts, and with the hydroxides of sulphur, before studying the oxides and hydroxides of this group.

oxygen readily to other substances with formation of hydro-chloric acid, thus :

$$ClOH = HCl + O.$$
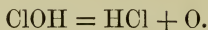
The most important salt of hypochlorous acid is calcium hypochlorite, which is continued in bleaching-powder.

Chlorous Acid, $HClO_2$.—This acid has not been isolated. When a solution of chlorine peroxide is treated with a base, a mixture of chlorite and chlorate is formed:

$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O.$$

The chlorites are unstable compounds. Chlorous anhydride, Cl_2O_3, has not been obtained. What was formerly regarded to be this compound has been shown to be a mixture of chlorine peroxide and chlorine.

Chlorine Peroxide, ClO_2, is a dark-yellow gas which condenses to red liquid, boiling at $9°$. It is obtained by adding potassium chlorate to oil of vitriol. In the reaction chloric acid is formed, and is decomposed at once into perchloric acid and chlorine peroxide:

$$KClO_3 + H_2SO_4 = HClO_3 + HKSO_4,$$
$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$
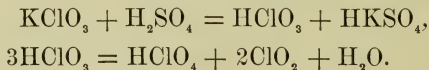
The preparation requires care, as the peroxide is explosive. The observed gas density of chlorine peroxide corresponds to the formula ClO_2. The following experiment illustrates the oxidizing action of the peroxide, and also the color of its solution:

Exp. 85.—Drop into a conical wine-glass filled with water a few crystals of potassium chlorate and a small bit of phosphorus. Pour some oil of vitriol, by means of a funnel tube, upon the chlorate. The phosphorus will burn under water, taking oxygen from the chlorine peroxide set free.

Chloric Acid, HClO₃ or ClO₂–OH, is best prepared by acting on barium chlorate with the requisite quantitiy of dilute sulphuric acid:

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$
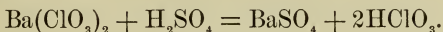
The barium sulphate is allowed to settle, and the clear solution is decanted and allowed to evaporate in vacuum over oil of vitriol. The residue remaining contains 40 per cent of $HClO_3$, and cannot be further evaporated without decomposition. The concentrated aqueous solution of chloric acid is colorless, has a strong acid reaction, and oxidizes paper, wood, and other organic substances.

Potassium Chlorate, KClO₃ or ClO₂–OK.—This salt is the most important of the chlorates. It is used in the manufacture of matches, in medicine, in explosive mixtures, and for other purposes. It is manufactured by passing chlorine gas into a hot mixture of lime, potassium chloride, and water:

$$KCl + 3CaO + 3Cl_2 = KClO_3 + 3CaCl_2.$$
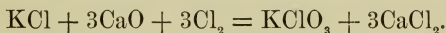
The chlorate is separated from the very soluble calcium chloride by crystallization.

When a solution of potassium hydroxide is saturated with chlorine, potassium hypochlorite and chloride are formed, thus:

$$2KOH + Cl_2 = KClO + KCl + H_2O.$$

If the solution is left for a day, or is boiled, the hypochlorite decomposes into chlorate and chloride:

$$3KClO = KClO_3 + 2KCl.$$

Potassium chlorate forms tabular crystals which are permanent in air. It is very soluble in hot water; but only 3.3 parts of the salt are soluble in 100 parts of water at 0°. The salt is decomposed by heat with evolution of oxygen; the

chemical changes involved in the reaction are given under potassium perchlorate.

Potassium chlorate yields its oxygen to combustible bodies more readily than potassium nitrate, and mixtures of it with sulphur, nitrobenzene ($C_6H_5NO_2$), or other substances explode with greater violence than gunpowder. Some of the mixtures containing chlorate are exploded by friction or percussion, and are used to fire gunpowder and other explosives.

Exp. 86.—Saturate with chlorine a solution made by dissolving 50 grams of potassium hydroxide in 150 cc. of water, and then boil a few minutes. Allow the solution to cool slowly; crystals of potassium chlorate will be deposited. Separate them from the mother-liquor, rinse once or twice with cold water; recrystallize by dissolving in a little more boiling water than required for solution, cool, and remove the crystals as before. Test them for potassium chloride by dissolving in water and adding a solution of silver nitrate. If the chlorate is free from chloride no precipitate will appear, as silver chlorate is soluble. Test the mother-liquor from the first crop of crystals for chlorine.

Exp. 87.—Mix cautiously on a paper equal bulks of powdered potassium chlorate and sugar. Place the mixture on a brick, under a hood, and drop upon it a little oil of vitriol.

Exp. 88.—Mix sulphur (flowers) with twice its bulk of pulverized potassium chlorate. Place as much of the mixture as can be held on the end of a penknife blade on an anvil, and strike with a hammer.

Perchloric Acid, $HClO_4$ or ClO_3–OH.—This acid is best prepared by distilling pure potassium perchlorate with four times its weight of concentrated sulphuric acid. At 110° the pure acid, $HClO_4$, distils over and condenses to a colorless or slightly yellow liquid. On continuing the distillation, the liquid which passes over changes to a crystalline mass of the hydrate, $HClO_4 + H_2O$, due to a partial decomposition of perchloric acid into oxides of chlorine and water, the latter uniting with the pure acid in the distillate.

Perchloric acid is a fuming, hygroscopic liquid, which explodes spontaneously when kept some days even in the dark. It decomposes with great violence when dropped upon

wood and charcoal. It forms with water crystals of the hydrate $HClO_4 + H_2O$, melting at 50°. Perchloric acid is a strong monobasic acid. Its salts, the perchlorates, require a higher temperature for their decomposition than the chlorates, and are, moreover, not decomposed by hydrochloric acid.

Potassium Perchlorate, $KClO_4$ or ClO_3–O–K.—When potassium chlorate is fused oxygen is evolved, and after a time the mass becomes pasty, and consists of potassium perchlorate, potassium chloride, with commonly some potassium chlorate. At a higher temperature the perchlorate is resolved into potassium chloride and oxygen. In order to prepare the perchlorate, the mixture obtained by cautiously heating potassium chlorate is allowed to cool, pulverized, and the greater part of the chloride dissolved out by water. The residue is then heated with hydrochloric acid, which converts any remaining chlorate, with evolution of chlorine and oxides of chlorine, into potassium chloride, which is finally removed by washing with water. Potassium perchlorate dissolves in 65 parts of water at 15°, and in much less boiling water.

Hypobromous Acid, HBrO, is similar in properties to its analogue, hypochlorous acid.

Bromic Acid, $HBrO_3$ or BrO_2–OH, is formed by the reaction of chlorine on bromine water, thus:

$$Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl.$$
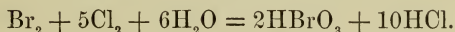
The acid is, however, best obtained by decomposing bromates. It is known only in aqueous solution, which is colorless, and which decomposes at 100°, with evolution of oxygen and bromine.

Iodine Trioxide, I_2O_3, is said to be formed, together with the pentoxide, by the action of ozone upon iodine.

Iodine Pentoxide, Iodic Anhydride, I_2O_5 or IO_2-O-IO_2, is obtained as a white powder by heating iodic acid to $200°$. It dissolves in water with formation of iodic acid.

Iodic Acid, HIO_3, or IO_2-OH, is prepared by dissolving iodine in fuming nitric acid, evaporating the solution, and heating the residue until all nitric acid is expelled. The product so obtained is dissolved in water, and from the solution rhombic crystals of the acid separate on evaporation.

Iodic acid is regarded by some writers as a bibasic acid, having the formula $H_2I_2O_6$, since it forms normal and acid salts, as for example, $K_2I_2O_6$, HKI_2O_6. Sulphur dioxide and hydrogen sulphide reduce iodic acid, with separation of iodine.

Periodic Acid, HIO_4, has not been isolated, but its salts have been prepared. The hydrate $HIO_4 + 2H_2O$, which may be viewed as monometaperiodic acid, $IO(OH)_5$, is formed by the action of iodine on perchloric acid:

$$ClO_3-OH + I + 2H_2O = IO(OH)_5 + Cl.$$

The acid is also formed by decomposing silver periodate with bromine. Monometaperiodic acid forms colorless deliquescent crystals, melting at $133°$, and decomposing at $140°$ into iodic anhydride, water, and oxygen. Periodic acid is remarkable for its complex salts, of which the following are examples: Ag_3IO_5, $Ag_3H_2IO_6$, $Ag_4I_2O_9$, and $Ba_5I_2O_{12}$.

Manganese Monoxide, Manganous Oxide, MnO or $Mn=O$, may be obtained by heating manganous carbonate in hydrogen. It is a grayish-green powder, which readily oxidizes when heated in air.

Manganous Hydroxide, $Mn(OH)_2$, forms a white, bulky precipitate on adding an alkali hydroxide to a solution of manganous chloride. It rapidly absorbs oxygen from the air,

and turns brown. It is a basic hydroxide, forming manganous salts with acids.

Manganous-Manganic Oxide, Mn_3O_4, occurs as the mineral hausmanite. This oxide is formed when any of the manganese oxides or manganous carbonate is strongly ignited in the air.

Manganic Oxide, or Manganese Sesquioxide, Mn_2O_3, occurs as braunite. The hydrate, or hydroxide, $Mn_2O_3 + H_2O = 2MnO-OH$, is the mineral manganite.

Manganese Dioxide, MnO_2, occurs as the mineral pyrolusite, and is commonly known as black oxide of manganese. It is used in the preparation of chlorine, and in the manufacture of glass to neutralize the color which iron imparts. Manganese dioxide is obtained artificially by igniting manganous nitrate. It separates as a hydrate on addition of a hypochlorite to a solution of manganese, and also when a dilute solution of manganese containing sodium acetate and a little free acetic acid is treated with chlorine or bromine. This last reaction is applied in the separation of manganese in chemical analysis.

Potassium Manganate, K_2MnO_4 or $MnO_2 {<}^{O-K}_{O-K}$. — When an oxide of manganese is fused with potassium hydroxide in contact with air, or better, mixed with potassium chlorate, a dark-green mass results. This forms with water a green solution, which on evaporation in vacuum deposits small crystals of potassium manganate, isomorphous with potassium sulphate. A better method for the preparation of the manganate is to boil a solution of potassium permanganate and potassium hydroxide as long as oxygen is evolved. The solution on cooling yields a powder which is dissolved in potassium hydroxide, and from this last solution almost black crystals

of the manganate separate.   Potassium manganate is decomposed by water, thus:

$$3MnO_2 \genfrac{}{}{0pt}{}{O-K}{O-K} + 2H_2O = 2MnO_3-O-K + 4K-OH + MnO_2.$$

Carbonic acid facilitates the change by combining with the potassium hydroxide to form carbonate.   In presence of sufficient alkali the decomposition does not occur.

Exp. 89.—Fuse on platinum foil sodium carbonate to which a very small quantity of an oxide of manganese has been added. Sodium manganate will be formed, and will color the mass a bright green. This is a delicate test for manganese.

Exp. 90.—To a concentrated solution of potassium hydroxide add a small crystal of potassium permanganate. The color of the solution of permanganate will change on warming to green, due to formation of manganate. Add more permanganate, and boil gently until the conversion into manganate is complete, shown by the pure green color of the solution, when some potassium manganate will separate. Pour the product into water. The dilute green solution, owing to the presence of excess of alkali, is tolerably permanent, but if sufficiently dilute will slowly change to red, owing to formation of permanganate. To the green solution of potassium manganate add an excess of sulphuric acid, and note change.

Potassium Permanganate, $KMnO_4$ or MnO_3-O-K, is obtained by decomposing potassium manganate as already described.   It forms dark-red crystals, which are isomorphous with potassium perchlorate, the two salts crystallizing together in all proportions. Potassium permanganate is soluble in about 16 parts of water at ordinary temperature. The solution, as well as the dry salt, is a powerful oxidizing agent, and on this account is employed as a disinfectant.

Ex. 91.—*a.* Dissolve a small quantity of oxalic acid in dilute sulphuric acid, and add drop by drop a solution of potassium permanganate until the red color of the permanganate is permanent. The reaction is represented as follows .

$$5 \; \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2MnO_3-O-K + 3SO_2 <^{OH}_{OH} =$$

$$SO_2 <^{O-K}_{O-K} + 2SO_2 <^{O}_{O} > Mn + 10CO_2 + 8H_2O.$$
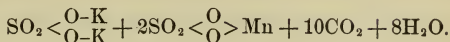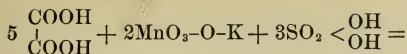
b. Add to river or spring water sufficient potassium permanganate to impart a reddish tint. After some days the color will disappear, owing to reduction of the permanganate by the organic matter in the water.

c. Leave a piece of paper for several days in a solution of potassium permanganate, and note change.

If dry potassium permanganate is added to well-cooled sulphuric acid, the latter is colored green, and, on adding more permanganate, **Manganese Heptoxide, Mn_2O_7,** separates as a heavy liquid, with a metallic, greenish lustre. Manganese heptoxide explodes with incandescence when heated. It forms a green solution with concentrated sulphuric acid, and dissolves in water to a red solution, probably of permanganic acid. When sulphuric acid containing an excess of potassium permanganate is cautiously heated to 50°, **Manganese Trioxide, MnO_3,** is evolved as a violet fume, which may be condensed to a dark-red liquid. It decomposes without incandescence when heated into manganese dioxide and oxygen. It forms an unstable red solution with water, which is supposed to contain manganic acid, H_2MnO_4.

Permanganic Acid, $HMnO_4$ or MnO_3-OH, is prepared by mixing barium permanganate with the required amount of sulphuric acid. The deep-red solution thus obtained decomposes on standing, quickly when heated, with evolution of oxygen and separation of hydrous manganese dioxide.

Permanganic Oxychloride, MnO_3Cl, is known. It is the chloranhydride of permanganic acid.

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Valence of the Elements of the Seventh Group, and Constitution of their Oxygen Compounds.

The halogens are univalent towards hydrogen and metals; in their oxygen compounds they exhibit higher valence.

Since all views of the valence of an element are based on the number of atoms in the molecules of its compounds, it is obvious that the hypothesis of valence can be strictly applied only to compounds whose molecular weights are known.

It is evident that if the number of atoms in a molecule of a given compound are unknown the valence assigned to the atoms becomes more or less hypothetical. Nevertheless it should be remembered that a constitutional formula in which the valence of atoms or groups of atoms (radicals) is implied or marked, thereby indicating its constitution or structure, represents more of the chemical properties of a compound than an empirical formula, that is, one which represents only the relative number of atoms in the compound.

Regarding valence as the capacity of an atom to hold other atoms in combination, we must assume that the valence of iodine in I_2O_5 is greater than in HI. Later we shall see that valence measured by oxygen may be higher than valence measured by hydrogen.

Oxygen acids are generally assumed to contain the radical hydroxyl, OH, that is, to be hydroxides. Proof of this will be given in the study of the constitution of sulphuric acid and organic acids. Viewing the oxy-acids of chlorine as hydroxides, we have the formulas

$$Cl–OH, \quad (ClO)–OH, \quad and \quad (ClO_2)–OH.$$

Chlorous acid may be represented by $\overset{\text{I}}{Cl}–O–OH$ or $O=\overset{\text{III}}{Cl}–OH$, according as we assume the chlorine in it to be a monad or a triad. In the first formula the radical hydroxyl is joined to oxygen, and in the second to chlorine. There are no reactions of the acid which support the constitution of either formula, but it is assumed that the hydroxyl is linked to chlorine, since, in other acids, for example those containing carbon, hydroxyl is not joined to oxygen. The argument

will be given later in the discussion of the constitution of carbon compounds.

Chlorine peroxide forms with water chlorous and chloric acids, and is therefore regarded as the mixed anhydride of these acids, thus :

$$O = \overset{\text{III}}{Cl}-O-\overset{\text{V}}{Cl}\lessgtr{}^{O}_{O} + H_2O \quad = \quad O = \overset{\text{III}}{Cl}-OH + {}^{O}_{O}\!\!\gtrless\overset{\text{V}}{Cl}-OH.$$

Chlorous chloric anhydride   Chlorous acid   Chloric acid

Bromic and iodic acids are probably analogous in constitution to chloric acid.

Perchloric acid crystallizes with one molecule of water, and the compound may be a trihydroxide, thus: ${}^{O}_{O}\!\!\gtrless\overset{\text{VII}}{Cl}\!\!\lessgtr{}^{OH}_{OH}$.

This constitution is doubtful, since no salts of a tribasic perchloric acid are known. The monobasic character of the acid is represented by the formula $\overset{\text{VII}}{Cl}\equiv\!\!\!\lessgtr{}^{OH}_{O}$

Orthoperiodic acid, $\overset{\text{VII}}{I}(OH)_7$, and its salts are unknown. Monometaperiodic acid, $O\overset{\text{VII}}{I}(OH)_5$, may be viewed as derived from the ortho-acid by the removal of the elements of one molecule of water, thus:

$$\overset{\text{VII}}{I}\!\!\!\equiv\!\!\!\lessgtr\begin{matrix}OH\\OH\\OH\\OH\\OH\\OH\\OH\end{matrix}-H_2O \quad = \quad \overset{\text{VII}}{I}\!\!\!\equiv\!\!\!\lessgtr\begin{matrix}OH\\OH\\OH\\OH\\OH\\O\end{matrix}$$

Orthoperiodic acid   Monometaperiodic acid
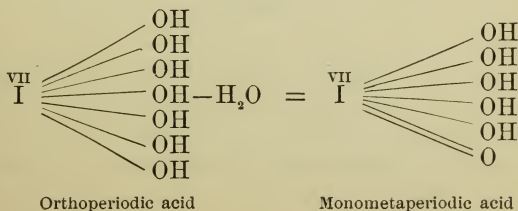
Dimetaperiodic acid and trimetaperiodic acid have not been isolated, but their salts have been prepared. The dimeta-acid may be regarded as derived from the monometa-acid, and the trimeta- from the dimeta-acid, thus:

| Monometaperiodic acid | Dimetaperiodic acid | Trimetaperiodic acid |
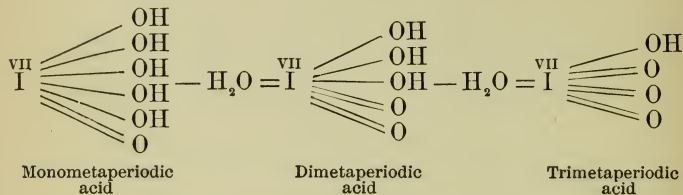
It has been stated that potassium perchlorate and potassium permanganate are isomorphous. It is therefore assumed that perchloric and permanganic acids have an analogous constitution. The anhydride of permanganic acid is Mn_2O_7, whose

structural formula is , on the assumption that
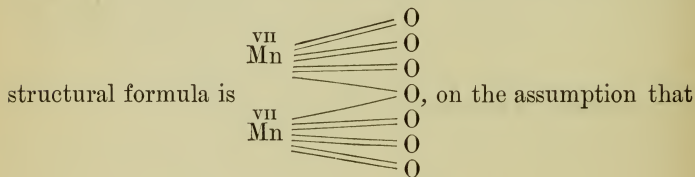
each oxygen atom is linked by two bonds to manganese.

Permanganic acid is
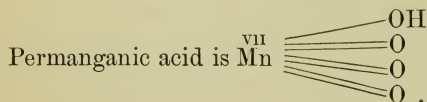
The structural formulas given of the oxy-acids of the seventh group are analogous to the formulas of ortho- and meta-acids of other elements, which will be studied later. Even if the foregoing formulas be considered as purely hypothetical, they will be found useful as an aid to the memory.

The student has only to recollect that an ortho-acid of a heptavalent element has seven hydroxyls, and that the meta-acids are derived from it by the withdrawal of the elements of one or more molecules of water.

The members of the seventh group exhibit in their different classes of compounds valence from one to seven, thus:

Fluorine, . . .	I				
Chlorine, . . .	I	III	V		VII
Bromine, . . .	I	III	V		
Iodine, ...	I		V		VII
Manganese, . .		II	IV	VI	VII

Summary of the Seventh Group.

It has been stated in the summary of the halogens that they exhibit decreasing affinity for hydrogen with increasing atomic weights; towards oxygen the reverse is true, viz., increasing affinity for oxygen with increasing atomic weights. Fluorine, with the lowest atomic weight in the group, does not unite with oxygen; and fluorine hydroxides are unknown.

In this connection it is to be further noticed, that oxides of iodine are more stable than those of chlorine. It is also remarkable that the stability of the oxy-acids of the halogens increases with the addition of oxygen. Thus hypochlorous acid, $ClOH$, is a weak acid, being liberated from its salts by carbonic acid; while perchloric acid forms stable salts, from which it is set free only by a strong acid, such as sulphuric. The following are the oxides and hydroxides of the seventh group:

Cl_2O. Hypochlorous anhydride	$ClOH$. Hypochlorous acid	No Oxides of Bromine	$BrOH$. Hypobromous acid	——	——	——	——
—	—	—	—	—	—	MnO. Manganous oxide	$Mn(OH)_2$. Manganous hydroxide
—	$ClO.OH$. Chlorous acid	—	—	I_2O_3.	—	Mn_2O_3. Manganic oxide	$MnO.OH$. Manganic hydroxide
ClO_2. Chlorine Peroxide	—	—	—	—	—	MnO_2. Manganese dioxide	—
—	$ClO_2.OH$. Chloric acid	—	$BrO_2.OH$. Bromic acid	I_2O_5. Iodic anhydride	$IO_2.OH$. Iodic acid	—	—
—	—	—	—	—	—	MnO_3. Manganic anhydride	$MnO_2(OH)_2$. Manganic acid
—	$ClO_3.OH$. Perchloric acid	—	—	—	$IO_3.OH$. Periodic acid	Mn_2O_7. Permanganic anhydride	$MnO_3.OH$. Permanganic acid

Chlorine, bromine, and iodine are closely related in chemical properties, and form a well-defined sub-group. Fluorine, with the lowest atomic weight in the group, stands apart from the other members in that it forms no oxides and hydroxides. The hydrogen compounds and the hydroxides of the halogens are acids, and do not possess any basic characteristics. Manganese, because of the magnitude of its atomic weight, is classed in the seventh group. It shows, however, relationship to the halogens only in permanganic acid and its salts. The lower oxides and hydroxides of manganese are basic compounds, forming salts with acids. The element in its basic character and metallic properties resembles iron. Manganese dioxide is an indifferent oxide, neither basic nor acidic. Manganic acid is analogous to sulphuric acid. The seventh group, therefore, presents marked analogies and great differences in properties.

The Oxides and Hydroxides of the First Group.

The hydroxides of the alkali metals are remarkable for their strongly basic properties and for their stability at high temperatures, not being decomposed into water and oxide even at a red heat. They constitute the caustic alkalies, so called from their caustic or corrosive properties. The oxides of copper and silver are more permanent than their hydroxides, and are strong basic oxides; but the hydroxides of gold are acids. The oxides of copper are not decomposed by ignition, while the oxides of silver and gold are reduced to the metals when heated.

The Oxides and Hydroxides of the Alkali Metals.

Lithium Oxide, Li_2O or Li–O–Li, is formed together with a higher oxide when lithium burns in the air. It may be prepared by igniting lithium nitrate. It is a white mass, which dissolves slowly in water with formation of the hydroxide.

Lithium Hydroxide, Li–OH, resembles the other alkali hydroxides, but does not absorb carbon dioxide as rapidly as, and, unlike potassium hydroxide, does not deliquesce in the air.

Sodium Monoxide, Na_2O or Na–O–Na, is best prepared by heating sodium hydroxide with sodium :

$$Na–OH + Na = Na–O–Na + H.$$
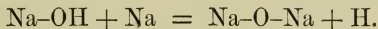
It unites energetically with water to form sodium hydroxide.

Sodium Dioxide, Na_2O_2, or Na–O–O–Na.—When sodium is burned in air both the monoxide and dioxide are formed. The dioxide is also obtained by heating sodium in oxygen until the mass ceases to increase in weight. If added gradually to water, sodium dioxide dissolves, and the solution on spontaneous evaporation yields crystals of $Na_2O_2 + 8H_2O$. When added to a small quantity of water, the mixture be-

comes hot, oxygen gas is evolved, and sodium hydroxide is formed.

Exp. 92.—Burn a piece of sodium the size of a pea on a porcelain crucible cover which is heated with a small lamp flame. When cool, place cover and contents in about 100 cc. of water; acidify the solution with hydrochloric acid, and test for hydrogen dioxide.

Express by an equation the reaction between the sodium dioxide and acid whereby hydrogen dioxide results.

Sodium Hydroxide, Sodium Hydrate, Caustic Soda, NaOH or Na–OH.—The cheap and common method of making caustic soda is by treating a boiling solution of sodium carbonate with slaked lime:

$$CO{<}{O-Na \atop O-Na} + Ca{<}{OH \atop OH} = 2Na{-}OH + CO{<}{O \atop O}{>}Ca.$$
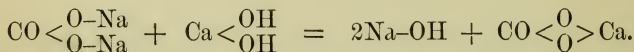
Sodium carbonate   Calcium hydroxide   Sodium hydroxide   Calcium carbonate

The insoluble calcium carbonate may be removed by filtration or be allowed to subside, and the clear liquid drawn off with a siphon. The solution is evaporated in an iron vessel, the heat being finally raised to a dull red, and the molten mass is cast into sticks or other convenient forms.

Pure sodium hydroxide is best obtained by dissolving metallic sodium in water, and evaporating the solution in a silver dish.

Sodium hydroxide is an opaque, brittle, white solid. It deliquesces in moist air, absorbs carbon dioxide, CO_2, and in time is completely changed to sodium carbonate, which remains as a white powder. When a solution of sodium hydroxide of density 1.385 is cooled below 0°, transparent crystals of the hydrate, $2NaOH + 7H_2O$, separate. From alcoholic solutions the hydrate, $NaOH + 2H_2O$, has been obtained.

Caustic soda is the cheapest of the alkalies, and is extensively used in the arts and in laboratories. Its aqueous solution is known as soda lye.

Exp. 93.—Slake 6 grams of quick-lime in 200 cc. of boiling water in a flask, and add 20 grams of crystallized sodium carbonate, $CO < {O-Na \atop O-Na} + 10H_2O$. Boil some minutes, then filter a portion, and to filtrate add an excess of hydrochloric acid. If gas (carbon dioxide) is given off the sodium carbonate has not all been converted into hydroxide, and a little more lime should be slaked in hot water, and the milk of lime added to the original portion and the whole boiled again. When a part of the clear solution does not evolve gas, on adding an excess of hydrochloride acid filter the solution into a jar. Try the action of the sodium hydroxide solution on the fingers.

To a solution of sodium carbonate add acid; the escaping gas is carbon dioxide. Test the white substance which remained on the filter when the sodium hydroxide was filtered for carbon dioxide, thus: Rinse some of it into a test-tube with a jet of water from the wash-bottle, then add hydrochloric acid.

Exp. 94.—*a.* Leave a small piece of sodium hydroxide exposed to the air in a porcelain dish for some days. Observe changes, and finally test for carbon dioxide.

b. Allow the solution of sodium hydroxide of the previous experiment to remain in an open jar several days, then test it for carbon dioxide.

Potassium Oxides.—Potassium burns in dry air with formation of a mixture of two oxides: the monoxide, K_2O or K–O–K, and the tetroxide, K_2O_4 or K–O–O–O–O–K. The monoxide resembles its sodium analogue in properties. The tetroxide has a dark-yellow color, and decomposes at a white heat into monoxide and oxygen. It dissolves in water with formation of potassium hydroxide, hydrogen dioxide, and free oxygen.

Potassium Hydroxide, Potassium Hydrate, Caustic Potash, KOH or K–OH, is prepared from potassium carbonate, $CO < {O-K \atop O-K}$, by treatment with lime in the same manner as sodium hydroxide.

Potassium hydroxide is white and brittle, and melts below a red heat. It absorbs water and carbon dioxide from the air, deliquescing, and forming potassium carbonate, which also

deliquesces if the air is not too dry. It dissolves in about half its weight of water, with evolution of much heat. The hot saturated solution deposits on cooling colorless crystals of the hydrate, $KOH + 2H_2O$, and the mother-liquor at ordinary temperature contains about 50 per cent of KOH. It is also soluble in alcohol. Solutions of potassium hydroxide are used to absorb carbon dioxide, and a saturated solution will remove water from gases.

Potassium hydroxide is a powerful base, combining with acids to form salts, and is used to separate other hydroxides from solutions of salts, as we shall learn by subsequent experiments. The aqueous solution of potassium hydroxide is frequently called potash lye. It corrodes animal and vegetable matter, and when concentrated cannot be filtered through paper. It is used in making soft soap.

Exp. 95.—Feel of a bit of caustic potash, and observe its corrosive action on the skin. Leave it in an open dish until it has deliquesced, then add to it a little water and an excess of hydrochloric acid. The escaping carbon dioxide was absorbed from the air.

Rubidium Hydroxide, Rb–OH, and **Cæsium Hydroxide, Cs–OH**, closely resemble potassium hydroxide.

The Oxides and Hydroxides of Copper, Silver, and Gold.

Copper Tetrantoxide, Cu₄O or $\begin{smallmatrix} Cu-Cu \\ | \\ Cu-Cu \end{smallmatrix} > O$, is an olive green powder, which absorbs oxygen from the air.

Cuprous Oxide, Cu₂O or $\begin{smallmatrix} Cu \\ | \\ Cu \end{smallmatrix} > O$, also called the red oxide of copper, may be obtained by heating finely divided copper

and cupric oxide in the proper proportions, and also by warming an alkaline solution of copper to which glucose or other reducing sugar has been added. This reaction is applied in the estimations of sugars.

Exp. 96.—To a few drops of a solution of cupric sulphate add a solution of potassium hydroxide until the precipitate of cupric hydroxide which first forms dissolves. Add a very little glucose or a drop of molasses, and boil the solution. The red precipitate is cuprous oxide. A yellow precipitate of hydrated cuprous oxide sometimes results.

Cupric Oxide, CuO or Cu = O.—When copper is heated in air it oxidizes, and on plunging the red hot metal into water the coating comes off. This is known as copper scale, and is a mixture of cuprous and cupric oxide. It is completely converted into cupric oxide by prolonged heating to redness in air or oxygen. On igniting cupric nitrate, $\dfrac{NO_2-O}{NO_2-O}>Cu$, cupric oxide remains as a black powder, which sinters together on heating more strongly. Cupric oxide fuses at a high red heat, with loss of oxygen, and is partly converted into cuprous oxide.

Hot copper oxide yields its oxygen readily to hydrogen and carbon, and is used in the combustion of compounds of these two elements in analysis.

Exp. 97.—Heat a piece of copper to redness and thrust it into water. Repeat several times. The scale will show both black and red oxide.

Exp 98.—Pass a very slow current of illuminating gas over glowing oxide of copper contained in a hard glass tube. The gas is a mixture of hydrogen, carbonic oxide, CO, and compounds of carbon and hydrogen. These substances are burned in the tube, and the products are water and carbon dioxide, CO_2, an invisible gas.

Cupric Hydroxide, Cu(OH)$_2$ or Cu$<\dfrac{OH}{OH}$.—When potassium hydroxide is added to a cold solution of a cupric salt a bulky

blue precipitate of cupric hydroxide is formed, which changes to cupric oxide on boiling the liquid.

Exp. 99.—Make cupric hydroxide, and heat cautiously to boiling. Represent changes by equations.

Copper Dioxide, CuO_2, is not known, but its hydrate, $CuO_2 + H_2O$, has been obtained.

Silver Tetrantoxide or Argentous Oxide, Ag_4O, and also some unstable argentous salts, have been prepared.

Silver Oxide, Argentic Oxide, Ag_2O or Ag-O-Ag.—This oxide is prepared by precipitating silver nitrate with potassium hydroxide. If the solutions are cold the precipitate is brown, and on drying becomes darker, while from hot concentrated solutions the oxide falls as a heavy black powder. Silver oxide decomposes completely below 300°, and yet is apparently formed to a slight extent when silver vapor cools in air. It is reduced by hydrogen at 100°. It is slightly soluble in water. The solution has a metallic taste and alkaline reaction, and may be assumed to contain silver hydroxide, $AgOH$. Moist silver oxide absorbs carbon dioxide from the air.

Exp. 100.—Dissolve 5 grams of silver nitrate in 100 cc. of water, add an excess of potassium hydroxide, wash the precipitate thoroughly on a filter, and dry it either at ordinary temperature or at 100°. Write the equation of the reaction. Heat a small portion of the oxide on the cover of a porcelain crucible.

Silver Dioxide, Ag_2O_2, is formed in the electrolysis of a concentrated solution of silver nitrate, and, according to Schoenbein, by the action of ozone on silver. Iles, by heating silver nitrate with silicic acid, has obtained a red modification, that made by electrolysis being black.

Aurous Oxide, Au_2O or Au-O-Au, is formed when aurous chloride is treated with a cold dilute solution of potassium hydroxide. It does not yield aurous salts, but with hydrochloric acid gives auric chloride and gold.

Auric Hydroxide, Au(OH)$_3$, is perhaps capable of separate existence; but Schrottlaender, in attempting to prepare it by decomposing gold trichloride with potassium hydroxide or auryl nitrate with water, obtained products which, after long drying, corresponded in composition fairly well with the following body:

Auryl Hydroxide, AuO.OH, or O = Au–OH.—This compound has been prepared by decomposing a dilute solution of auric chloride with sodium hydroxide, and then adding sodium sulphate, which separates the hydroxide as a dark-brown precipitate (Thomsen). Auryl hydroxide at 200° loses water, with formation of **Auric Oxide, Au$_2$O$_3$,** which loses all its oxygen at a higher temperature. The hydroxide dissolves in acids, yielding auryl salts, in which the basic radical may be regarded as –Au=O.

Potassium Aurate, AuO.OK or O = Au–O–K, is obtained in yellow crystals with three molecules of water, by dissolving auryl hydroxide in a slight excess of pure potassium hydroxide, and evaporating the solution. The salt is not very stable, is easily soluble in water, and is used for gilding.

The compounds of gold thus far considered show that the metal is basic or acidic in its nature, according as it is united with strongly acidic or basic elements. For example, it is basic in AuCl$_3$, and acidic in AuO.OK.

SULPHUR, SELENIUM, AND TELLURIUM.

Sulphur, S.

Atomic Weight, 32.   *Molecule,* S_2.

Native sulphur is abundant in many volcanic regions, and is often found in beautiful rhombic crystals. It occurs in combination with many metals, as in lead sulphide, PbS, and iron sulphide, FeS_2, and is a constituent of many other minerals. Sulphur compounds are present in many animal and vegetable substances, and in natural waters.

The process of extracting native sulphur is simple. The ore is heated until the sulphur melts and flows from the admixed earthy substances. The crude sulphur thus obtained is purified by distillation. If the vapor is conducted into a cool chamber, a fine yellow powder falls, which is known as flowers of sulphur. When the chamber becomes hot only liquid sulphur collects, and this is cast in wooden moulds, and is known as roll sulphur or brimstone.

Sulphur exists in several allotropic forms.

Rhombic Sulphur is found in transparent yellow octahedrons, variously modified. It is obtained by the slow evaporation of a solution of sulphur in carbon disulphide, and forms when sulphur vapor or a large mass of molten sulphur cools slowly. Rhombic sulphur has a density at 0° of 2.05, and melts at 114°.5, forming a yellow liquid having a density of 1.803. It is very soluble in carbon disulphide, but slightly soluble in alcohol and insoluble in water.

Exp. 101.—Dissolve sulphur in carbon disulphide, and filter the solution into a beaker. Cover the beaker with paper to keep out dust, and also to insure slow evaporation, and leave it under a hood or out of doors until the solvent has evaporated.

Monoclinic Sulphur.—If molten sulphur is allowed to cool in the air until it has partly solidified and the liquid is then poured off, long delicate crystals will be seen, which are deeper-colored than the rhombic crystals of the foregoing experiment. This modification is not permanent; and the crystals in a few days, and often in a few hours, become opaque, owing to a change to an aggregation of minute crystals of the rhombic form. Monoclinic sulphur melts at 120°, has a density of 1.96, and is soluble in carbon disulphide. The solution yields rhombic crystals when evaporated.

Exp. 102.—Allow molten sulphur contained in a beaker to cool, watch the growth of the crystals, and when there has formed on the surface of the sulphur a crust, make a hole in it and pour the liquid portion into a porcelain dish. The crust may be cut away with a knife. Compare the crystals with those of the previous experiment. Keep the sulphur in the beaker for a few days until it has become opaque. The portion in the porcelain dish when solid will have the color of the crystals, and in fact will be a mass of crystals, and will also undergo the same change.

Amorphous Soluble Sulphur.—When an acid is added to a solution of an alkali polysulphide, sulphur separates in exceedingly fine particles. This form, which is known as milk of sulphur, is white, and is soluble in carbon disulphide. Under the microscope it appears to be non-crystalline.

Exp. 103.—Dissolve some flowers of sulphur in a hot concentrated solution of potassium hydroxide, dilute the solution with water, and add an excess of hydrochloric acid. If the liquid containing the milk of sulphur is poured upon a filter, some of the finely divided sulphur will pass through the pores of the paper. The composition of the sulphides of potassium will be given later.

Amorphous Insoluble Sulphur.—Sulphur separates in a yellow plastic amorphous form, insoluble in carbon disulphide, when a chloride of sulphur is decomposed by water or a solution of a thiosulphate by hydrochloric acid. A plastic form, also insoluble in carbon disulphide, is obtained by quickly cooling sulphur which has been heated to near its boiling point. Thus obtained it may be drawn into threads. It becomes hard and brittle in a few days. When flowers of sulphur are treated with carbon disulphide a part remains undissolved.

Sulphur at temperatures but little higher than its melting point is a pale-yellow liquid, which gradually becomes dark red and viscid on heating, and at 200° to 250° is too thick to pour readily. On increasing the temperature the sulphur grows less viscid, but remains dark-colored. Sulphur boils at 448°.4, under a pressure of 760 mm. The density of sulphur vapor diminishes with increasing temperature, but has been found constant between 860° and 1040°, and to be 32, corresponding to the gas molecule S_2. At 518° a density of 96 has been observed, indicating the existence of molecules of S_6. Blitz has, however, found that when sulphur is mixed with nitrogen, its density at 518° is from 65 to 71. This result, together with the fact that the density is not constant at moderate intervals of temperature between 500° and 600°, renders doubtful the existence of gas molecules of S_6.

Exp 104.—Melt clean pieces of roll sulphur in a test-tube, with care not to heat the sulphur much above its melting point, so as to obtain a thin yellow liquid, and pour a few drops into water. These will be brittle. Next heat the sulphur until it will not pour from the tube, then heat to boiling, and pour in a thin stream into water. Set aside a part of the plastic sulphur obtained, and after some days note any change.

Selenium, Se.

Atomic Weight, 79.   *Molecule,* Se_2.

This element occurs sparingly in nature.   It is obtained in the manufacture of sulphuric acid from pyrites which contain traces of it.   Selenium, like sulphur, exists in different modifications.   When molten selenium is quickly cooled, an amorphous, almost black mass results, soluble in carbon disulphide. From such a solution small dark monoclinic crystals, of density 4.5, separate on evaporation.   When an aqueous solution of selenious acid is treated with sulphur dioxide, selenium separates as a red powder, which is also soluble in carbon disulphide. Metallic and insoluble selenium results when molten selenium is very slowly cooled.   It has a lead-gray metallic lustre, and is a conductor of electricity.   Its density is 4.5, and it melts at 217°.   Minute black crystals of selenium, having a density of 4.8, separate when a strong solution of potassium selenide is exposed to air.   This black modification is also insoluble in carbon disulphide.

Selenium boils below 700°.   Its gas density at 1400° corresponds to the molecule Se_2.   Selenium burns in air with a blue flame, and with a characteristic odor, said to resemble that of rotten horse-radish.

Tellurium, Te.

Atomic Weight, 125.   *Molecule,* Te_2.

Tellurium is found in nature in small quantity, both free and in combination.   It has a bluish-white metallic lustre, and a density of 6.24.   It melts at about 500°, and may be distilled

in hydrogen gas. Its gas density at 1390° has been found to be 131.6. Tellurium is insoluble in carbon disulphide. When ignited in air it burns with formation of the dioxide.

The elements oxygen, sulphur, selenium, and tellurium exhibit gradations in physical properties which are related to their atomic weights. Oxygen, which stands apart in chemical properties, likewise shows the greatest variation in physical properties, and possesses no metallic characteristics, while tellurium has the properties of a metal.

	Oxygen.	Sulphur.	Selenium.	Tellurium.
Atomic weight,	16	32	79	125
Gas density, .	16–24	32	79	125
Density, .	1.12 liquid	1.96–2.05	4.5–4.8	6.2
Melting point, .	——	114–120°	217°	500°
Boiling point, .	−181°	448°	below 700°	Red heat.

Hydrogen Sulphide, Sulphuretted Hydrogen, H_2S or H–S–H, is a colorless gas, occurring in many mineral waters commonly called sulphur waters, to which it imparts medicinal properties. It is formed in the decay of various organic substances containing sulphur, and to it is due in part the odor of rotten eggs. Hydrogen unites with boiling sulphur to form hydrogen sulphide, but the amount obtained is small. The common method of making hydrogen sulphide is to act on ferrous sulphide with dilute hydrochloric or sulphuric acid. The following equations represent the changes :

$$Fe{=}S + 2HCl = S{<}^{H}_{H} + Fe{<}^{Cl}_{Cl.}$$

$$Fe{=}S + SO_2{<}^{OH}_{OH} = S{<}^{H}_{H} + SO_2{<}^{O}_{O}{>}Fe.$$
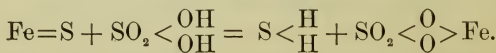
The gas thus prepared contains a little hydrogen set free from the acid by particles of metallic iron in the ferrous sul-

phide ordinarily used. If native antimony trisulphide is employed, pure hydrogen sulphide will be obtained.

The gas density of hydrogen sulphide is 17 ; its molecular weight is therefore 34. Analysis has shown that there are 32 weights of sulphur and 2 weights of hydrogen in 34 weights of hydrogen sulphide. Hence its molecule is H_2S.

Hydrogen sulphide condenses to a liquid, boiling at $-62°$ and solidifying at $-85°$. Water at common temperature dissolves about three volumes of the gas. The solution reacts slightly acid, and has the odor and sweetish taste of the gas. Hydrogen sulphide is readily decomposed by heat and by oxidizing agents. Its aqueous solution gradually becomes turbid in contact with air owing to separation of sulphur and formation of water, thus :

$$H_2S + O = H_2O + S.$$
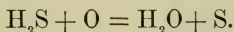
Nitric acid, chlorine, and bromine decompose hydrogen sulphide. The reaction with chlorine is expressed by the equation—

$$H_2S + Cl_2 = S + 2HCl.$$
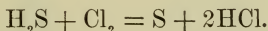
Hydrogen sulphide is very inflammable, burning with a blue flame with formation of water and sulphur dioxide, SO_2:

$$H_2S + 3O = H_2O + SO_2.$$
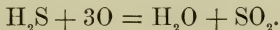
If the supply of air is not sufficient for complete combustion part of the sulphur separates. Hydrogen sulphide is much used in analytical chemistry for the precipitation of various metals as sulphides. Sulphuretted hydrogen is poisonous to inhale, and air containing a little of it produces nausea and headache.

Exp. 105.—The Kipp apparatus, Fig. 74, is one of the most convenient forms of generators for the preparation of hydrogen sulphide. The globe A contains ferrous sulphide. The acid employed is common

muriatic acid, diluted with twice its bulk of water. The wash-bottle
contains water to free the gas from any solution carried over. Instead
of a Kipp generator, a bottle such as is used in Exp. 6, Fig. 52, will
answer.

Allow hydrogen sulphide to bubble slowly through distilled water in
a bottle until, on closing the bottle with the thumb and shaking, the gas
is no longer absorbed. Keep the solution for later experiments.

Exp. 106 —*a*. Pass hydrogen sulphide through a hot tube. *b*. Fill a
tall cylinder with the gas and ignite it.
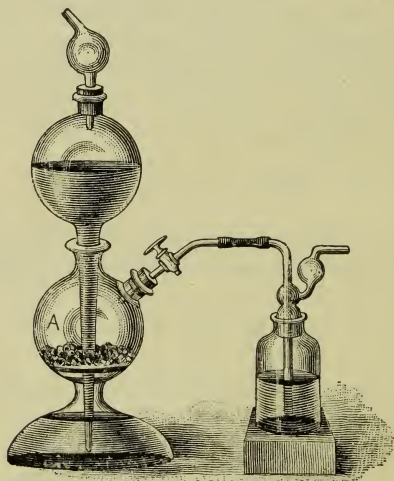
Fig. 74.

Exp. 107.—*a*. Add to a solution of hydrogen sulphide chlorine or bro-
mine water, and (*b*) to another portion its bulk of concentrated nitric acid.

Exp. 108.—*a*. Treat a solution of cupric sulphate containing hydro-
chloric acid with an excess of hydrogen sulphide. The following is
the reaction:

$$SO_2 <^O_O> Cu + S <^H_H = Cu = S + SO_2 <^{OH}_{OH}.$$
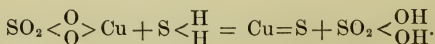
b. Add hydrogen sulphide to a solution of zinc sulphate to which a

little hydrochloric acid has been added. Note the result. Next add to the solution ammonia in excess. The white precipitate is zinc sulphide.

c. Pass hydrogen sulphide into a solution containing copper sulphate, zinc sulphate, and some hydrochloric acid. After the copper is all precipitated, filter, and add to the clear colorless filtrate ammonia to alkaline reaction. Some zinc sulphide will be precipitated, and more will separate on adding hydrogen sulphide.

The separation of copper from zinc in the experiment illustrates the use of hydrogen sulphide in chemical analysis.

Exp. 109.—*a.* Dissolve arsenious oxide in hot strong hydrochloric acid, but do not boil the mixture, as a volatile poisonous arsenic compound will be given off. Pour the solution into water, and add hydrogen sulphide. The precipitate is arsenic trisulphide.

b. Dissolve tartar emetic, an antimony salt, in water, and add some tartaric acid and hydrochloric acid, and then hydrogen sulphide. The precipitate is antimony trisulphide.

Hydrogen Disulphide, H_2S_2, is the analogue of hydrogen dioxide. It is an unstable yellow liquid, which slowly decomposes into hydrogen sulphide and sulphur.

Hydrogen Selenide, H_2Se, and **Hydrogen Telluride, H_2Te,** are gases which closely resemble in chemical properties their analogue, hydrogen sulphide.

Sulphur Monochloride, S_2Cl_2, is made by passing chlorine over sulphur gently heated in a retort. The chloride distils over, and is purified by redistillation. It is a yellow liquid, boiling at 138°. Its gas density has been found to be 68.8, showing that its molecule is S_2Cl_2. It dissolves two thirds of its weight of sulphur. Sulphur monochloride gradually decomposes in contact with water, thus:

$$2S_2Cl_2 + 2H_2O = 4HCl + SO_2 + 3S.$$
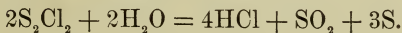
Sulphur chloride is employed in vulcanizing rubber.

Sulphur Dichloride, SCl_2, is formed when chlorine acts on the monochloride at a temperature of 6° to 10°. It decomposes on heating into monochloride and chlorine.

Sulphur Tetrachloride, SCl$_4$, is formed when chlorine is passed into the dichloride cooled to $-22°$. The liquid obtained evolves chlorine as soon as the temperature rises.

The compounds S$_2$Br$_2$, S$_2$I$_2$, and SI$_6$ have been obtained.

A number of halides of selenium and tellurium are known. Tellurium tetrachloride boils without decomposition at 380°. The density of its gas has been found to be 130 at 448°; theory requires 133 for TeCl$_4$. The tetrachlorides of sulphur and selenium dissociate on heating.

The Sulphides and Hydrosulphides of the First Group.

Potassium Hydrosulphide, K–S–H.—A solution of this substance is obtained by saturating a solution of potassium hydroxide with hydrogen sulphide. The liquid is colorless, strongly alkaline, and on evaporation out of contact with air deposits colorless crystals of the compound 2KSH + H$_2$O. A solution of potassium hydrosulphide decomposes gradually on exposure to air, becoming yellow, and after a time colorless.

Potassium Monosulphide, K$_2$S or K–S–K, is obtained by saturating one half of a solution of potassium hydroxide with hydrogen sulphide and then adding the remaining half of the solution of potassium hydroxide. The solution absorbs oxygen from air, and becomes yellow owing to formation of higher sulphides.

Potassium trisulphide, K$_2$S$_3$; potassium tetrasulphide, K$_2$S$_4$; and potassium pentasulphide, K$_2$S$_5$, are known. The latter compound is easily obtained by heating a solution of any of the other sulphides with flowers of sulphur.

The potassium sulphides are decomposed by acids with evolution of hydrogen sulphide, and excepting KSH and K_2S, with separation of sulphur, as shown in Exp. 103.

Sodium Sulphides are similar to the potassium sulphides and are prepared by the same methods.

Cuprous Sulphide, Cu_2S or $\dfrac{Cu}{Cu}{>}S$, is formed when copper is burned in sulphur, and remains as a brittle dark gray mass when cupric sulphide is strongly ignited in hydrogen. Native cuprous sulphide or chalcocite occurs in handsome crystals of a blackish lead-gray color. It is an important ore of copper.

Exp. 110.—Place in a narrow glass tube six inches long and closed at one end some sulphur and a copper wire. Heat strongly until the copper ceases to glow in the sulphur vapor. When cool examine the product.

Cupric Sulphide, $Cu{=}S$, is obtained by the action of hydrogen sulphide on cold solutions of cupric salts as a bulky black precipitate (see Exp. 108, *a*). While moist it readily oxidizes, with formation of cupric sulphate. If the precipitation is made in a boiling solution the cupric sulphide is denser, and easier to filter. The precipitated sulphide becomes blue on gentle ignition out of contact with air, and at higher temperatures loses half its sulphur.

Silver Sulphide, Ag_2S or Ag–S–Ag.—The native sulphide, known as argentite, occurs widely distributed as an ore. Silver sulphide is formed by the direct union of its elements, and by the action of hydrogen sulphide upon the metal. It separates as a blackish-brown precipitate on addition of hydrogen sulphide to a solution of a silver salt.

Exp. 111.—Expose a clean silver coin to hydrogen sulphide gas or solution. The reaction is represented by the equation—

$$2Ag + H{-}S{-}H = Ag{-}S{-}Ag + H_2.$$
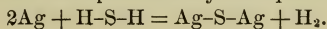
Gold Sulphides.—When an acid or neutral solution of gold is treated with hydrogen sulphide a black precipitate results, which, according to some experimenters, is a mixture of gold sulphide or sulphides with free sulphur and occasionally metallic gold. The precipitate is soluble in solutions of alkali sulphides. When sodium sulphide is used the following compound is formed :

Sodium Aurous Sulphide, $Na–Au=S + 4H_2O$, is prepared by strongly heating gold with sodium sulphide, treating the fused mass with water, and evaporating the solution out of contact with oxygen. It forms colorless monoclinic prisms, which become brown in the air.

The Oxides and Hydroxides of Sulphur, Selenium, and Tellurium.

Four compounds of sulphur and oxygen are known, namely : the sesquioxide, S_2O_3 ; the dioxide, SO_2 ; the trioxide, SO_3 ; and the heptoxide, S_2O_7.

Sulphur Sesquioxide, S_2O_3.—When flowers of sulphur are gradually added to sulphur trioxide, dark-blue drops of the sesquioxide form, which at once solidify. The sesquioxide decomposes slowly at ordinary temperature, more readily on warming, into sulphur dioxide and sulphur. It dissolves in fuming sulphuric acid to a blue solution.

Sulphur Heptoxide, S_2O_7, is formed when electric sparks are passed through a mixture of sulphur dioxide and oxygen. It separates in oily drops, which solidify at $0°$. It decomposes spontaneously, quickly on warming, into sulphur trioxide and oxygen.

Sulphur Dioxide, Sulphurous Oxide or Anhydride, SO_2.—This substance is formed when sulphur burns in air or oxygen. That sulphur dioxide contains its own volume of oxygen may be shown by the following experiment :

Exp. 112.—Through the stopper of the apparatus, Fig. 75, pass two stout wires, one of which is fastened to the handle of the platinum spoon B, and the other is connected by means of a piece of blowpipe platinum wire with the inside of the bowl of the spoon, so that the small platinum wire may be made to glow by means of a current from a battery. A bit of sulphur is melted about the connecting wire in the spoon. The apparatus is filled with dry oxygen by passing the gas through it for a few minutes. The stopper is then put in place and mercury poured in, the stopper being loosened to allow the mercury to stand at the same height in both limbs. The apparatus should stand some time after filling, so that it may have the temperature of the room. When ready to try the experiment, add or draw off mercury till it stands at the same height in both limbs ; then draw off a third or more of the mercury into an empty beaker to rarefy the gas in the bulb, and close the opening C with a cork. Connect for an instant the wires in A with a battery. The glowing platinum wire will inflame the sulphur. After the flame has disappeared remove the cork from C and pour back the mercury which was drawn off to diminish pressure. When the apparatus has cooled to the temperature of the room it will be found that the gas occupies a little less space than the original oxygen. The slight diminution in volume is due to the fact that when sulphur burns in oxygen or air a small quantity of sulphur trioxide forms, which is not gaseous at ordinary temperature. The cloud seen in the bulb is not sulphur dioxide, but trioxide, or if moisture is present it is sulphuric acid.
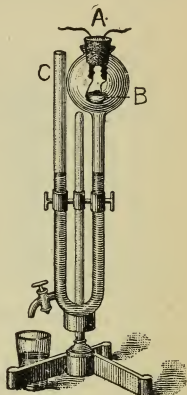
Sulphur dioxide is prepared in several ways. A good method for obtaining the pure gas depends upon the decomposition of hot sulphuric acid by copper, represented by the following equation:

$$2SO_2 <{OH \atop OH} + Cu = SO_2 + SO_2 <{O \atop O}> Cu + 2H_2O.$$
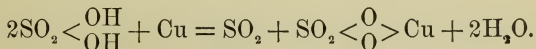
A little copper sulphide is formed at the same time. In case

FIG. 75.

the presence of carbon dioxide is not objectionable, charcoal may be used to advantage:

$$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O.$$

Sulphur dioxide is a colorless gas, which is easily liquefied when exposed to low temperature or pressure. The liquid boils at $-8°$, and when a strong blast of air is directed against its surface a portion of the dioxide freezes to a snow-like mass, melting at about $-80°$. The vapor of pure sulphur dioxide mixed with air is rather less irritating when inhaled than the fumes from burning sulphur, which are chiefly sulphur dioxide, but also contain a little sulphuric acid formed at the same time. The observed gas density of sulphur dioxide is 32. Hence its molecular weight is 64. Exp. 112 shows that one volume of sulphur dioxide gas contains one volume of oxygen.

One volume of sulphur dioxide gas weighs 32
"   "   " oxygen weighs. 16
                                                                              ——
Weight of sulphur in one volume of sulphur dioxide . 16

Hence sulphur dioxide is composed of equal weights of sulphur and oxygen, and in the molecular weight, 64, there are 32 weights of sulphur, the weight of one atom, and 32 weights of oxygen, the weight of two atoms. Therefore the molecular formula is SO_2.

Sulphur dioxide is used in bleaching silk, wool, and straw, in place of chlorine, which injures these materials. It is a valuable disinfectant, and for this purpose and also for bleaching it is obtained by burning sulphur.

Exp. 113.—Heat a flask containing copper clippings and strong sulphuric acid, and pass the gas through water to free it from sulphuric acid fume, and then into distilled water until a saturated solution is ob-

tained.   The sulphur dioxide gas may be collected over mercury or by displacing air.   If liquid dioxide is desired, the gas should be dried by passing it through concentrated sulphuric acid, and then into a test-tube immersed in a freezing mixture of ice and salt.   The apparatus shown in Fig. 76 is convenient.   The liquid dioxide which collects in A may be drawn off by opening the pinchcock B. The tube C is held in a freezing mixture in a beaker.   It is filled about two thirds with liquid dioxide, and without removing it from the freezing mixture is sealed by drawing off the neck in the flame of a blast-lamp.   A number of tubes may be successively filled and kept until needed. A tube containing the dioxide should be cooled before breaking open the narrow end.

Exp. 114.—Water may be frozen in a red-hot dish as follows.   Heat a platinum capsule two inches in diameter by means of a good lamp to bright redness, and drop into it cautiously from a small test-tube a little liquid sulphur dioxide ; then pour in about the same bulk of water.   The capsule is at once seized with tongs and the ice thrown upon a piece of wood.   The liquid dioxide assumes the spheroidal state in the hot dish and does not boil, being separated from the metal

FIG. 76.

by a layer of gaseous dioxide.   When the water is added the agitation causes the liquid dioxide to boil violently, and the heat required for vaporization is taken in part from the water which is frozen.

Exp. 115.—Place a little liquid sulphur dioxide on a large watch-glass, and direct a current of air from a bellows on it.   The white, snow-like mass obtained will gradually disappear without melting.

Sulphurous Acid, H_2SO_3, $SO(OH)_2$ or $H-SO_2-OH$.—Water dissolves about 40 volumes of sulphur dioxide at ordinary temperature.   The acid has not been isolated, but is assumed to exist, because the solution reacts acid, and yields with bases sulphites.   Dry sulphur dioxide does not redden blue litmus paper.   A solution of sulphurous acid gradually absorbs oxygen from the air, with formation of sulphuric acid.   A
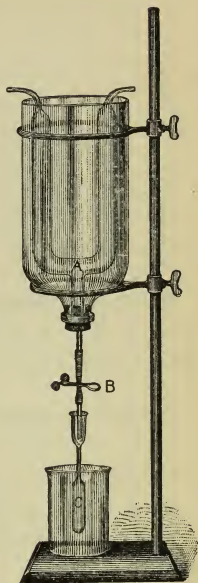
number of reactions in which the same change is effected are given under Sulphuric Acid.

The constitution of sulphurous acid has been the subject of careful investigations, which cannot be given here. The results thus far obtained indicate that $H-SO_2-OH$ is the structural formula. According to this view, two acid sodium (or potassium) salts are possible, $Na-SO_2-OH$ and $H-SO_2-ONa$. Since it is not known which of these formulas represent the constitution of hydrogen sodium sulphite, the empirical formula $HNaSO_3$ will be used.

Hydrogen Sodium Sulphite, $HNaSO_3$.—This salt separates when a cold concentrated solution of sodium carbonate is saturated with sulphur dioxide, carbon dioxide being evolved.

Sodium Sulphite, Na_2SO_3.—To prepare this substance sodium carbonate is saturated with sulphur dioxide, and to the solution as much more sodium carbonate is added. The anhydrous salt separates when the saturated solution is heated.

The potassium salts $HKSO_3$ and K_2SO_3 are analogous to the sodium sulphites.

The sulphites are decomposed by acids, with evolution of sulphur dioxide.

Sulphur Trioxide or Sulphuric Anhydride, SO_3 or $SO_2=O$.—When dry sulphur dioxide and oxygen are passed over hot platinum sponge the two gases unite to form sulphur trioxide. It is more easily obtained by gently warming fuming sulphuric acid in a retort, and receiving the vapors in a flask. Thus prepared it contains a trace of water, melts at $16°$, and boils at about $46°$. On standing at ordinary temperature long crystalline fibres slowly form, which fuse above $50°$, and change to the first-mentioned form. According to Weber, perfectly pure sulphur trioxide fuses at $14°.8$ and boils at $46°.2$, and is changed by a small amount of moisture into the fibrous modification.

Sulphur trioxide fumes in the air, and unites with water to form sulphuric acid. Its gas density corresponds to the molecule SO_3.

Sulphuric Acid, H_2SO_4 or $SO_2{<}^{OH}_{OH}$.—This acid is more extensively used than any other acid. It is manufactured on an enormous scale by the so-called lead-chamber process. Sulphur dioxide, from burning sulphur or iron pyrites, FeS_2, is passed into large lead chambers, into which are also conducted air, steam, and fumes of nitric acid. The complicated changes which occur may in part be represented as follows:

Sulphur dioxide is converted into sulphuric acid by the nitric acid, which is reduced to nitrogen dioxide, NO_2, thus:

$$SO_2 + 2NO_2{-}OH = SO_2{<}^{OH}_{OH} + 2NO_2.$$
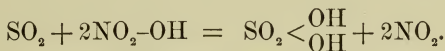
The nitrogen dioxide in presence of water converts another portion of sulphur dioxide into sulphuric acid :

$$SO_2 + NO_2 + H_2O = SO_2{<}^{OH}_{OH} + NO.$$
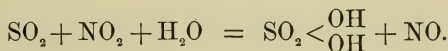
The nitrogen monoxide takes oxygen from the air supplied, and is changed to the dioxide :

$$NO + O = NO_2.$$
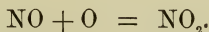
Thus small quantities of the oxides of nitrogen serve as carriers of oxygen, and suffice for the conversion of a large quantity of sulphur dioxide into sulphuric acid. The dilute chamber acid is evaporated in lead pans until it contains about 78 per cent of H_2SO_4, stronger acid attacking the lead. It is then further concentrated in glass or platinum retorts. The crude concentrated acid is commonly called oil of vitriol.

Sulphuric acid may be detected by means of barium chloride, $Ba<_{Cl}^{Cl}$, which forms with it and also with solutions of sulphates a white precipitate of barium sulphate, $SO_2<_O^O>Ba$, which is insoluble in acids.

Exp. 116.—Dilute a few drops of sulphuric acid largely with water and add a solution of barium chloride. Try to dissolve the precipitate obtained with hydrochloric acid. Formulate the reaction.

Exp. 117.—Burn sulphur in a jar of air, or better, oxygen, and then pour in some barium chloride. The slight turbidity indicates that a little sulphuric acid is formed when sulphur burns. Next place in the jar a strip of wood moistened with concentrated nitric acid. Red fumes will be seen, also more barium sulphate.

Exp. 118.—To sulphur dioxide obtained by burning sulphur in oxygen add bromine water. The color of the bromine will disappear.

$$SO_2 + Br_2 + 2H_2O = SO_2<_{OH}^{OH} + 2HBr.$$
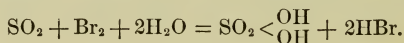
Test for the presence of sulphuric acid. Chlorine in presence of water also converts sulphur dioxide into sulphuric acid.

The oil of vitriol of commerce is frequently dark-colored from organic matter, contains lead sulphate, and often other impurities. It is purified by distilling in glass. The most concentrated acid that can be obtained by distillation contains about 2 per cent of water. If such acid is cooled, crystals of H_2SO_4 separate, which are free from water. These melt at $10°.5$, and remain liquid when cooled below this temperature. The pure liquid acid has a density of 1.854 at $0°$. Ordinary concentrated sulphuric acid or oil of vitriol having a density of 1.819 at $15°$ contains 89.7 per cent of acid. The pure acid fumes when warmed, part of the H_2SO_4 being dissociated into sulphur trioxide and water, and on heating to $338°$, the boiling point of the liquid, an acid remains containing 1.2 to 1.6 per cent of water, and which distils unchanged.

The density of the vapor obtained by heating sulphuric acid to 440° has been found to be 25, which corresponds to that of a mixture of equal molecules of water and sulphur trioxide and shows that sulphuric acid does not exist in the gaseous state.

When sulphuric acid is mixed with water much heat is evolved, the mixture at the same time undergoing contraction. The acid absorbs moisture rapidly from the air, and is therefore used for drying gases. Oil of vitriol chars wood and paper, and burns the skin.

Exp. 119.—Pour a thin stream of oil of vitriol into water. The heating of the mixture will be evident. Water should not be poured into the acid, owing to the danger of the acid being thrown out by sudden bursts of steam. If oil of vitriol contains lead sulphate, this will separate as a white precipitate when the acid is diluted with water.

Exp. 120.—Place in a test-tube oil of vitriol and pieces of cloth, paper, and wood, and after some days observe the result.

BASES, ACIDS, AND SALTS.

THE oxides and hydroxides of the metals possess, as a rule, the property of neutralizing acids. This peculiar property is termed basic. The oxides which exhibit it are called basic oxides, and the hydroxides are called bases. Later we shall learn that some metallic hydroxides are acids. Soluble bases turn red litmus blue, having what is called an alkaline reaction. Acids, on the contrary, redden blue litmus, and decompose carbonates with evolution of carbon dioxide. There are many compounds which are neither acids, bases, nor salts ; but the distinguishing characteristics of strong bases and acids are easily recognized.

Let us next consider the constitution of two bases with which we are already familiar, namely, potassium hydroxide and sodium hydroxide.

If we regard oxygen as bivalent and potassium and hydrogen as univalent, we may represent potassium hydroxide by the structural formula K–O–H. Sodium hydroxide may be likewise represented as Na–O-H. The group OH is called hydroxyl, and has already been noticed under hydrogen dioxide. It is an example of a compound radical.

Radicals.—A simple radical is a single atom. A compound radical is a group of atoms which deports itself like a single atom, and which may be transferred from one compound to another without losing its identity. Thus OH may be regarded in K–OH as replacing Cl in K–Cl. Compound as well as simple radicals possess valence. Later we shall become acquainted with a number of compound radicals.

Chemists regard oxygen acids as hydroxides, that is, compounds containing the radical OH. The structural formula of sulphuric acid is $SO_2 < {OH \atop OH}$. This represents the acid as containing the radicals SO_2 and OH. Later it will be seen that the properties of sulphuric acid are best indicated by the structural formula, which is therefore more useful than the simpler one, H_2SO_4.

In the electrolysis of sodium chloride sodium appears at the negative electrode and is therefore electro-positive, and chlorine is disengaged at the positive electrode and is electro-negative. A solution of potassium sulphate is decomposed by electricity, with formation of potassium hydroxide at the negative and sulphuric acid at the positive electrode. Since salts are thus separated into positive and negative parts in electrical relations, the former being basic and the latter acidic, it is customary to call basic radicals positive radicals, and acid radicals negative radicals. Potassium chloride, KCl, contains the positive radical K, the same that in KOH gives it basic properties. Hydrogen is common to both acids and bases, and is regarded as possessing neither acidic nor basic properties. Assuming that sulphuric acid contains two hydroxyls, the negative radical is either S, SO or SO_2; the latter is considered to be the acid radical, and is termed sulphuryl.

Salts are regarded as built on the same plan as the acids from which they are derived. Thus the structural formula of potassium sulphate is $SO_2 < {O-K \atop O-K}$. Nitric acid is NO_2-O-H and potassium nitrate is NO_2-O-K, NO_2 being the acid radical. The formulas in the following equations of the formation of salts represent similarity in the structure of oxygen bases, acids, and salts, in this respect, that in these three classes of compounds radicals are linked together by oxygen:

$$K\text{--}O\text{--}H + NO_2\text{--}O\text{--}H = NO_2\text{--}O\text{--}K + H\text{--}O\text{--}H;$$

$$K\text{--}O\text{--}H + SO_2{<}{O\text{--}H \atop O\text{--}H} = SO_2{<}{O\text{--}K \atop O\text{--}H} + H\text{--}O\text{--}H;$$

$$2K\text{--}O\text{--}H + SO_2{<}{O\text{--}H \atop O\text{--}H} = SO_2{<}{O\text{--}K \atop O\text{--}K} + 2H\text{--}O\text{--}H.$$
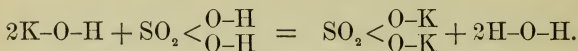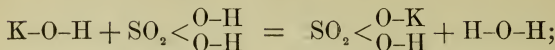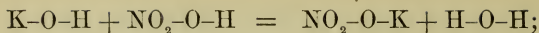
From the structural formulas of bases, acids, and salts the following definitions are derived :

An oxygen base consists of a positive (basic) radical joined by oxygen to hydrogen.

An oxygen acid consists of a negative (acid) radical joined by oxygen to hydrogen.

An oxygen salt consists of a positive radical or radicals joined by oxygen to a negative radical or radicals.

The formation of salts by the reaction between acids and bases is always accompanied by the elimination of water.

Sulphuric acid contains two atoms of hydrogen, which may be replaced by metals. This property is indicated by calling it a dibasic acid. Two molecules of potassium hydroxide, $K\text{--}O\text{--}H$, are required to saturate it, and but one is needed to saturate monobasic nitric acid, $NO_2\text{--}O\text{--}H$. In the same way potassium hydroxide is considered a monacid base; calcium hydroxide (slaked lime) a diacid base, since it reacts with two molecules of a monobasic acid, or one of a dibasic acid, to form a salt, thus:

$$Ca{<}{O\text{--}H \atop O\text{--}H} + 2H\text{--}Cl = Ca{<}{Cl \atop Cl} + 2H\text{--}O\text{--}H;$$

$$Ca{<}{O\text{--}H \atop O\text{--}H} + 2NO_2\text{--}O\text{--}H = Ca{<}{O\text{--}NO_2 \atop O\text{--}NO_2} + 2H\text{--}O\text{--}H;$$

$$Ca{<}{O\text{--}H \atop O\text{--}H} + SO_2{<}{O\text{--}H \atop O\text{--}H} = Ca{<}{O \atop O}{>}SO_2 + 2H\text{--}O\text{--}H.$$
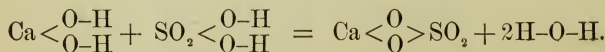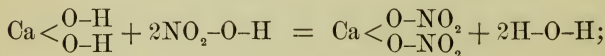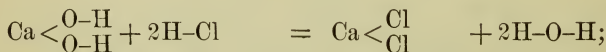
It is evident that the basicity of an acid is indicated by the valence of the acid radical, and the acidity of a base by the valence of the basic radical. The same may be expressed differently, as follows:

An acid is mono-, di-, tri-, or more basic according as it contains one, two, three, or more atoms of hydrogen joined by oxygen to the acid radical.

A base is mono-, di-, tri-, or more acid according as it contains one, two, three, or more hydrogen atoms joined by oxygen to the basic radical.

Normal Salts are those in which the bonds of the acid radical or radicals equal the bonds of the basic radical or radicals. Potassium nitrate, NO_2–O–K, and potassium sulphate, $SO_2 {<}{\begin{smallmatrix} O-K \\ O-K \end{smallmatrix}}$, are examples.

Acid Salts are those in which the bonds of the acid radical exceed the bonds of the basic radical or radicals, as for example in hydrogen potassium sulphate, $SO_2 {<}{\begin{smallmatrix} O-K \\ O-H \end{smallmatrix}}$.

Basic Salts are those in which the bonds of the basic radical or radicals exceed the bonds of the acid radical. For instance, basic lead nitrate, ${\begin{smallmatrix} NO_2-O \\ H-O \end{smallmatrix}}{>}Pb$.

Acid Anhydrides.—Oxides which combine with water to form acids are termed acid anhydrides. For example, sulphuric anhydride, SO_3, and water unite to form sulphuric acid. The acid anhydrides are derived from acids by the removal of the elements of water:

$$H_2SO_4 - H_2O = SO_3.$$

Salts result from a number of reactions of a different character from those already stated. They are formed by the replacement of the hydrogen of an acid by a metal,

$$Zn + SO_2 <^{O-H}_{O-H} = SO_2 <^O_O> Zn + H_2;$$
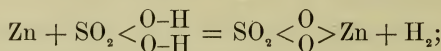
by the combination of an acid anhydride with a metallic oxide,

$$SO_2 = O + Ca = O = SO_2 <^O_O> Ca;$$
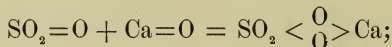
by the reaction between a metallic oxide and an acid,

$$Ca = O + SO_2 <^{O-H}_{O-H} = SO_2 <^O_O> Ca + H-O-H;$$
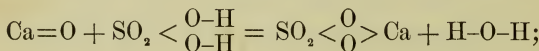
and also by an exchange of radicals between two salts,

$$SO_2 <^{O-K}_{O-K} + Ba <^{Cl}_{Cl} = SO_2 <^O_O> Ba + 2K-Cl.$$
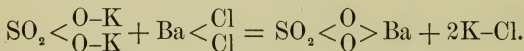
Sulphuryl Hydroxychloride or Sulphuric Hydrochloride, $SO_2 <^{Cl}_{OH}$.—This compound is formed by the direct union of sulphuric anhydride and hydrochloric acid. It is best obtained by heating a mixture of sulphuric acid and phosphorus oxychloride :

$$2SO_2 <^{OH}_{OH} + POCl_3 = 2SO_2 <^{Cl}_{OH} + HPO_3 + HCl.$$
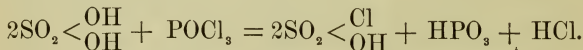
Phosphorus oxychloride is used to effect the replacement of hydroxyl by chlorine in a number of reactions. Sulphuryl hydroxychloride is a colorless fuming liquid, boiling at 158°.

Its gas density accords with its formula. It is decomposed violently by water, with formation of sulphuric and hydrochloric acids. Hence it may be viewed as a chloranhydride of sulphuric acid.

Sulphuryl Chloride or Sulphuric Dichloride, $SO_2 <^{Cl}_{Cl}$.—Sulphur dioxide and chlorine unite in sunlight to form this substance. It is, however, best prepared by heating sulphuryl hydroxychloride in a sealed tube to 180° for twelve hours:

$$2SO_2 <^{Cl}_{OH} = SO_2 <^{Cl}_{Cl} + SO_2 <^{OH}_{OH}.$$
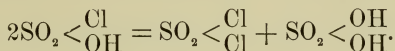
Sulphuryl chloride is a colorless liquid, boils at 70°, and has a gas density of 67.5. It yields with little water sulphuryl hydroxychloride and hydrochloric acid, and with an excess of water sulphuric and hydrochloric acids. It is, therefore, a chloranhydride of sulphuric acid.

Constitution of Sulphuric Acid.—The chloranhydrides of sulphuric acid are formed, as already shown, by the replacement of oxygen and hydrogen by chlorine. The simplest supposition is that the acid contains the radical hydroxyl, OH; a view supported by the reactions of the chloranhydrides with water, whereby an atom of chlorine is replaced by the elements of hydroxyl. The changes may be represented thus:

$$SO_2 <^{\boxed{Cl + H}-O-H}_{Cl} = SO_2 <^{O-H}_{Cl} + H-Cl.$$

$$SO_2 <^{O-H}_{\boxed{Cl + H}-O-H} = SO_2 <^{O-H}_{O-H} + H-Cl.$$
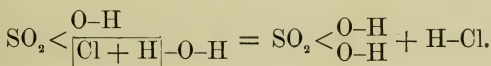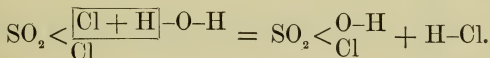
Both changes may occur simultaneously:

$$SO_2 <^{\boxed{Cl + H}-O-H}_{\boxed{Cl + H}-O-H} = SO_2 <^{O-H}_{O-H} + 2H-Cl.$$
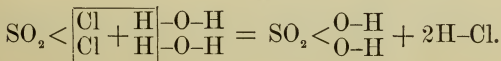
It may be stated that there are many reactions analagous to the foregoing in which chlorine replaces hydroxyl, and that proof of the presence of hydroxyl in a compound is found in such reactions.

If we accept the structural formula of sulphuryl chloride we see that the foregoing equations are simple expressions of the nature of the reactions. Further, the formula $SO_2 {<} {OH \atop OH}$ represents the relation of sulphuric acid to the chloranhydrides derived from it. The mutual relation between the sulphur atom and two of the oxygen atoms is different from that of the oxygen atoms in the hydroxyl group, and these last two are influenced by or united to both sulphur and hydrogen. These supposed differences in the relations of the atoms in the molecule are indicated by the formula

$${O \atop O}{>\!\!\!=}\, S {<} {O-H \atop O-H}.$$

Sulphur Hexhydroxide or Orthosulphuric Acid, $S(OH)_6$.— When sulphuric acid, H_2SO_4, is mixed with water in the proportion of one molecule of the former to two of the latter the contraction in bulk is greater than with other proportions. It is supposed that the compound H_6SO_6 ($= H_2SO_4 + 2H_2O$) is formed. Its only structural formula appears to be

$$S {\Huge <} \begin{matrix} OH \\ OH \\ OH \\ OH \\ OH \\ OH \end{matrix}$$
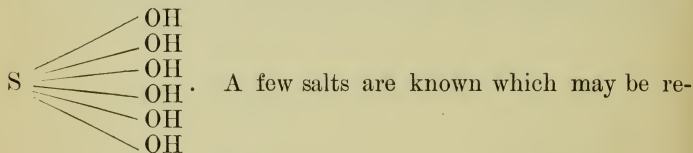
A few salts are known which may be regarded as derivatives of this acid; for example, the mercury sulphate,

$$S {\Huge <} \begin{matrix} {O \atop O} {>} H_g \\ {O \atop O} {>} H_g \\ {O \atop O} {>} H_g \end{matrix}.$$

Monometasulphuric Acid, $SO(OH)_4$.—When a mixture of equal molecules of sulphuric acid and water is cooled, crystals having the composition $H_2SO_4 + H_2O$ form. These melt at $7°.5$. Monometasulphuric acid is derived from orthosulphuric acid by the removal of one molecule of water, giving the formula

$$S \begin{cases} OH \\ OH \\ OH \\ OH \\ O \end{cases}$$ By taking away another molecule of
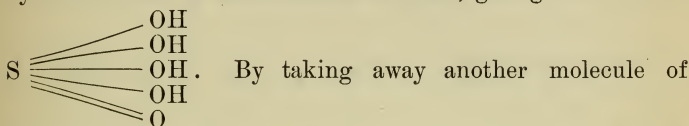
water, ordinary or dimetasulphuric acid results, and this in turn yields sulphuric anhydride by further dehydration. This hypothesis of the derivation of acid hydroxides accords with the theory of valence, and is a help in studying them.

Disulphuric Acid, $H_2S_2O_7$ or $\begin{matrix} SO_2 < ^{OH}_{O} \\ SO_2 < ^{OH} \end{matrix}$.—This acid is formed from sulphuric acid by the removal of water, thus:

$$\begin{matrix} SO_2 <^{OH}_{OH} \\ SO_2 <^{OH}_{OH} \end{matrix} - H_2O = \begin{matrix} SO_2 <^{OH}_{O} \\ SO_2 <^{OH} \end{matrix}.$$
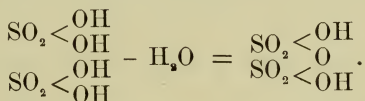
Disulphuric acid forms well-defined salts, is dibasic, fumes in the air, and decomposes on warming into sulphur trioxide and sulphuric acid. The fuming sulphuric acid of commerce is a mixture of sulphuric and disulphuric acids. It is manufactured from iron pyrites, FeS_2, by a process of roasting and distilling, and is also obtained by adding sulphur trioxide to sulphuric acid. The chloranhydride of disulphuric acid, $\begin{matrix} SO_2 <^{Cl}_{O} \\ SO_2 <^{Cl} \end{matrix}$, is known.
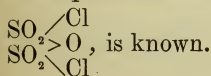
Thiosulphuric Acid, $H_2S_2O_3$ or $SO_2 <^{OH}_{SH}$.—This acid, as its name indicates, may be regarded as sulphuric acid with an

oxygen atom replaced by sulphur. The free acid is unknown, as it immediately decomposes when liberated from its salts into sulphur and sulphur dioxide, thus :

$$SO_2 {<}^{OH}_{SH} = H_2O + SO_2 + S.$$
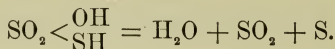
Sodium Thiosulphate, $Na_2S_2O_3 + 5H_2O$ or **$SO_2 {<}^{O-Na}_{S-Na} +$ $5H_2O$.**—This salt is more commonly known as hyposulphite of soda. It is obtained by boiling a solution of sodium sulphite with flowers of sulphur, when the following reaction occurs :

$$Na_2SO_3 + S = Na_2S_2O_3.$$
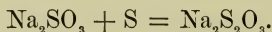
Other methods are also used in manufacturing it.

Sodium thiosulphate forms large transparent monoclinic crystals, which are permanent in the air and very soluble in water. It is used in the manufacture of paper as an antichlor, in photography, and as a reagent in the laboratory.

Hyposulphurous Acid, H_2SO_2 or **$SO {<}^{H}_{OH}$.**—Zinc dissolves in a solution of sulphurous acid without evolution of hydrogen, and with formation of hyposulphurous acid. The yellow solution which results possesses greater bleaching power than sulphurous acid. If a solution of acid sodium sulphite is treated with zinc, there is formed, together with other products, sodium hyposulphite, $SO {<}^{H}_{ONa}$. This compound is used in calico-printing. From the hyposulphite the free acid is liberated by oxalic acid. The solution obtained has a deep orange color, and decomposes quickly with separation of sulphur. The acid is monobasic. Solutions of its salts on exposure to air absorb oxygen with formation of sulphites.

Dithionic Acid, $H_2S_2O_6$; Trithionic Acid, $H_2S_3O_6$; Tetrathionic Acid, $H_2S_4O_6$; and **Pentathionic Acid, $H_2S_5O_6$,** have long been known.

Selenium Dioxide, SeO_2.—This is the only known oxide of selenium. It is prepared by burning selenium in a current of

dry oxygen. It forms needle-like crystals, which volatilize without fusion at about 300°. The dioxide is the acid anhydride of selenious acid.

Selenious Acid, H_2SeO_3 or $SeO{<}^{OH}_{OH}$, separates in colorless crystals on cooling a solution of five parts of selenium dioxide in one part of hot water. It forms salts which are analogous to the sulphites. It also forms compounds with an acid selenite, such as, $HKSeO_3 + H_2SO_3$.

Selenic Acid, H_2SeO_4 or $SeO_2{<}^{OH}_{OH}$, is prepared by decomposing silver selenite, suspended in water, by bromine :

$$Ag_2SeO_3 + Br_2 + H_2O = H_2SeO_4 + 2AgBr.$$
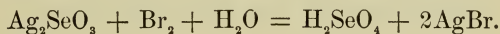
The insoluble silver bromide is removed, and the solution is concentrated by evaporation.

The acid dissolves zinc and iron with evolution of hydrogen, and when hot and concentrated it dissolves gold with reduction to selenious acid.

Tellurium Dioxide, TeO_2, is formed when tellurium burns in air. It is but slightly soluble in water, and the solution does not react acid to litmus. It possesses feeble basic as well as acidic properties.

Tellurium Trioxide, TeO_3, results when telluric acid is heated to a temperature below a red heat. It has an orange-yellow color, and is insoluble in water, in cold hydrochloric acid, and a solution of potassium hydroxide, unless the latter is hot and concentrated.

Tellurous Acid, H_2TeO_3 or $TeO{<}^{OH}_{OH}$, separates when a solution of tellurium chloride is poured into water, in which

the acid is but slightly soluble. The salts K_2TeO_3, $HKTeO_3$, and $K_2TeO_3.3TeO_3$, are examples of tellurites.

Telluric Acid.—When a dilute solution of this acid is evaporated, crystals having the composition of $Te(OH)_6$ separate. This is the analogue of orthosulphuric acid. The crystals lose water at 160°, and change into H_2TeO_4. Telluric acid forms salts analogous to the sulphates, and also such acid compounds as $K_2TeO_4 + 3TeO_3 + 4H_2O$.

Sulphates of the First Group.

Sodium Sulphate, Na_2SO_4 or $SO_2{<}{{O-Na}\atop{O-Na}}$.—This salt is made commercially in enormous quantities by heating common salt with sulphuric acid. It is also obtained in the manufacture of nitric acid from sodium nitrate. It occurs in many natural waters. The crude sodium sulphate of commerce is known as "salt cake," and is one of the intermediate products in the manufacture of sodium carbonate from sodium chloride. It is used in glass-making.

When a solution of sodium sulphate evaporates at ordinary temperature, the decahydrated salt $Na_2SO_4 + 10H_2O$, commonly known as Glauber's salt, separates in colorless monoclinic crystals. The crystals effloresce in dry air, melt at 33°, and give up all their water below 100°. The heptahydrated salt $Na_2SO_4 + 7H_2O$ sometimes separates in hard rhombic crystals when a supersaturated solution of sodium sulphate is cooled. This hydrate is sometimes sold for Glauber's salt.

Sodium sulphate dissolves to the greatest extent in water when the mixture is warmed to 34°, at which temperature a saturated solution contains 50 parts of Na_2SO_4 in 100 parts of

water. On heating such a solution monohydrated sodium sulphate will separate. Pulverized Glauber's salt and strong hydrochloric acid make a convenient freezing mixture. The salt $Na_2SO_4 + 7H_2O$ will not answer instead of Glauber's salt.

Exp. 121.—Make a solution by heating to 34° on a water-bath a mixture of 125 cc. of water and $\frac{1}{2}$ k. of Glauber's salt in a flask. Shake frequently, and when no more appears to dissolve filter the solution into a flask. Cover the neck of the flask with paper to keep out dust. Allow the solution to cool to common temperature, when it will be supersaturated, that is, will contain more of the salt than is ordinarily soluble. Next drop into the solution a fragment of Glauber's salt. Crystals will grow very rapidly. Dust from the air will also cause crystals to form, owing, perhaps, to minute particles of sodium sulphate in the air.

Hydrogen Sodium Sulphate, Acid Sodium Sulphate, HNaSO$_4$ or $SO_2 < {}^{O-Na}_{O-H}$.—This salt separates in crystals when a solution of equal molecules of sulphuric acid and sodium sulphate is evaporated by heat.

Sodium Disulphate or Pyrosulphate, Na$_2$S$_2$O$_7$ or ${SO_2 \atop SO_2} {{>}\!\!\!\!< \atop } {{O-Na} \atop {O \atop O-Na}}$. —This compound results from heating the preceding salt. It is best prepared by heating a mixture of sodium sulphate and sulphuric acid until the mass fuses quietly at a dull-red heat. At higher temperatures SO_3 is evolved, leaving Na_2SO_4.

Potassium Sulphate, K$_2$SO$_4$ or $SO_2 < {}^{O-K}_{O-K}$, crystallizes in small rhombic pyramids. The salt is soluble in 10 parts of water at ordinary temperature. It is obtained from certain minerals and as a by-product in some chemical manufactures. It is used in making potash-alum, and other potassium compounds.

Hydrogen Potassium Sulphate, HKSO$_4$ or SO$_2<^{O-K}_{O-H}$, may be prepared by melting together 13 parts of potassium sulphate with 8 parts of oil of vitriol. It is soluble in about half its weight of boiling water, and the solution on cooling deposits rhombic crystals. It is decomposed by a large quantity of water, and the dilute solution when evaporated deposits first crystals of the normal salt, then crystals having the composition **K$_2$SO$_4$ + HKSO$_4$,** and finally hydrogen potassium sulphate.

Potassium Disulphate, K$_2$S$_2$O$_7$, is similar in properties to sodium disulphate, and is prepared in a like manner.

Hydrogen Potassium Disulphate, HKS$_2$O$_7$ or $^{SO_2}_{SO_2}>^{/O-K}_{\backslash OH}$.— This compound is obtained in crystals by dissolving potassium disulphate in fuming sulphuric acid.

Hydrogen potassium sulphate and potassium disulphate and the corresponding sodium salts are valuable as fluxes. At a red heat they convert into sulphates oxides or salts which are not affected by boiling sulphuric acid.

Lithium Sulphate crystallizes with one molecule of water, while **Rubidium** and **Cæsium Sulphates,** like the potassium sulphate, form only anhydrous salts. The salts, HLiSO$_4$, HRbSO$_4$, and HCsSO$_4$ are known.

Cupric Sulphate, Copper Sulphate, CuSO$_4$ or SO$_2<^O_O>$ Cu. —This salt is manufactured on a large scale by roasting ores containing copper sulphide and lixiviating with water. The solution yields on evaporation blue crystals having the composition CuSO$_4$ + 5H$_2$O, which are known in commerce as blue vitriol and blue-stone. It is also made by dissolving copper

scale in sulphuric acid. The crystallized salt loses four mole-
cules of water at 100°, becoming greenish white, and the last
molecule at 200°, becoming pure white in color. The com-
position of the monohydrate is that of monometa-sulphate,
$\dfrac{HO}{HO} > SO < \dfrac{O}{O} > Cu$. The anhydrous $CuSO_4$ absorbs water on
exposure to moist air, and becomes blue. When intensely
ignited it is changed into cupric oxide. Both the hydrous
and anhydrous salt absorb hydrochloric acid gas with forma-
tion of cupric chloride and sulphuric acid. This reaction is
made use of in separating hydrochloric acid gas from other
gases. One part of $CuSO_4 + 5H_2O$ is soluble in about $2\frac{1}{2}$
parts of water at ordinary temperature, and one half a part at
100°. The salt is insoluble in alcohol. Blue vitriol is the most
common of copper salts. It is used in dyeing, in preparing
other copper compounds, in electroplating, and electrotyping,
and in galvanic batteries.

Exp. 122.—Heat powdered blue vitriol until the residue is white. Ex-
pose a portion of the anhydrous sulphate to the air, add another portion to
common alcohol, and agitate. In both cases the sulphate will become
blue—a proof of the presence of water in the air and alcohol.

Silver Sulphate, Ag_2SO_4 or $SO_2 < \dfrac{O-Ag}{O-Ag}$.—Silver like copper
dissolves in hot oil of vitriol with the evolution of sulphur di-
oxide. This fact is applied in separating gold from silver in
alloys, the silver dissolving in the sulphuric acid and the gold
remaining. Silver sulphate requires 88 parts of boiling water
and about 200 parts of cold water to dissolve it. It is much
more soluble in water containing nitric acid or sulphuric acid.
Silver sulphate separates as a white powder when sulphuric
acid is added to a not too dilute solution of silver nitrate. It
fuses at a dull-red heat, and at a higher temperature decom-
poses into silver, oxygen, and sulphur dioxide.

Hydrogen Auryl Sulphate, HAuOSO$_4$ or **O=Au–O–SO$_2$OH**. —This compound is formed when auryl nitrate or hydroxide is digested at 200° with concentrated sulphuric acid. The crystalline meal which separates is freed from the mother-liquor on a porous plate, washed with nitric acid, density 1.49, and dried over lime. The salt has a canary-yellow color, is very hygroscopic, and is decomposed by water into auryl hydroxide and sulphuric acid. The hydrogen of this salt may be replaced by potassium forming the compound KAuOSO$_4$.

Gold Sulphate, AuSO$_4$, is formed by the rapid evaporation of a solution of auryl sulphate at 250°, and separates in scarlet-red prisms which absorb moisture and become black. The salt is decomposed by water with formation of the compound Au$_6$H$_4$O$_8$ = 6AuO + 2H$_2$O.

CHROMIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM.

Chromium, Cr.

Atomic Weight, 52.5.   *Density*, 6.8.

Chromium was discovered independently by Vauquelin and Klaproth in 1797.   The chief source of chromium is chromite, $FeCr_2O_4$. Metallic chromium is prepared by intensely heating the oxide with charcoal, or by reducing the chloride with zinc at high temperatures.   It has been obtained by these methods only in the form of powder or small crystals.   The metal is deposited in the electrolysis of its chloride as glistening scales or a coherent plate. It is more infusible than platinum, and as hard as corundum.   The pure metal is more permanent in damp air than iron. It is soluble in hydrochloric and sulphuric acid, but not in nitric acid.

Chromium forms compounds corresponding to CrO, Cr_2O_3, and CrO_3.   The first two are basic oxides, and the last is an acid anhydride.

Chromous Compounds.

Chromous Chloride, $CrCl_2$ or $Cr{<}^{Cl}_{Cl}$.—This compound is obtained by heating chromic chloride in hydrogen, and also by dissolving metallic chromium in hydrochloric acid.   Chromous chloride oxidizes readily, and is an energetic reducing agent.

Chromous Hydroxide, $Cr(OH)_2$, separates when potassium hydroxide is added to a solution of chromous chloride. It absorbs oxygen on exposure to air. When heated it is converted into chromic oxide with liberation of hydrogen:

$$2Cr(OH)_2 = Cr_2O_3 + H_2 + H_2O.$$
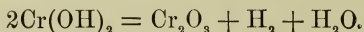
Chromous Sulphate, $CrSO_4 + 7H_2O$.—This salt forms blue crystals. Like other chromous compounds it quickly oxidizes in the air.

Chromic Compounds.

Solutions of chromic salts have a violet color, which changes to green on heating. Green solutions become violet on long standing at common temperature. The different colors of the solutions have been ascribed to two modifications of chromic salts. Recent investigations indicate that when a violet solution of a chromic salt becomes green on heating, the normal salt decomposes into a basic salt and free acid.

Chromium Sesquioxide, Chromic Oxide, Cr_2O_3 or $O = Cr-O- Cr = O$.—This oxide is obtained by igniting chromic hydroxide as an amorphous green powder, and in dark-green crystals by passing chromyl chloride through a red-hot tube. Chromium sesquioxide fuses in the flame of the compound blowpipe, and solidifies on cooling to a dark crystalline mass, which is sufficiently hard to scratch glass and steel.

Chromium sesquioxide is used to impart a green tint to glass and porcelain, and as a green pigment in paints.

It dissolves slowly in hot sulphuric acid, and is insoluble in other acids. When ignited with alkalies in contact with air it absorbs oxygen with formation of chromates.

Chromic Hydroxides.—Ammonia produces in a green solution of a chromic salt a grayish-green and in a violet solution a grayish-blue precipitate, which, after drying over sulphuric acid, has the composition $Cr(OH)_3 + 2H_2O$. This compound loses water readily, and is converted, as already stated, into anhydrous oxide by ignition. Potassium and sodium hydroxides throw down from a solution of a chromic salt a green hydroxide containing alkali. The precipitate dissolves in excess of alkali to a deep-green solution, from which on long standing or boiling chromic hydroxide separates.

Chromic Chloride, $CrCl_3$, is obtained by passing chlorine over an intensely heated mixture of chromic oxide and charcoal. It is nearly insoluble in pure water, but dissolves easily to a green solution in water containing a little chromous chloride. A solution of chromic chloride is also obtained by dissolving chromic hydroxide in hydrochloric acid.

$$\text{Chromic Sulphate, } Cr_2(SO_4)_3 \text{, or } \begin{matrix} SO_2 <_O^O \searrow \\ SO_2 <_O^O \\ SO_2 <_O^O \nearrow \end{matrix} \begin{matrix} Cr \\ \\ Cr \end{matrix}$$
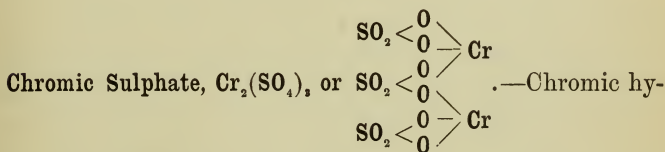
.—Chromic hydroxide dissolves in strong sulphuric acid to a green solution, which does not yield a violet crystalline precipitate on adding alcohol. On long standing in moist air the solution absorbs water and changes to a crystalline mass, which dissolves in water to a violet solution, from which alcohol precipitates the hydrate $Cr_2(SO_4)_3 + 18H_2O$. Chromic sulphate and alkali sulphates form alums, of which the following is the most common.

Potassium Chromic Sulphate, Chrome Alum, $K_2SO_4 . Cr(SO_4)_3$ $+ 24H_2O$.—This double salt is easily made by adding sul-

phuric acid to a solution of potassium dichromate and some reducing agent, such as sulphur dioxide or alcohol. The solution on standing several days deposits ruby-red octahedrons. The salt is used in dyeing.

Compounds of Hexvalent Chromium.

Chromium Hexfluoride, CrF$_6$ or $F \diagdown Cr \diagup F$, with F and F above and F and F below —This compound is prepared by heating in a retort a mixture of lead chromate, fluor spar, and fuming sulphuric acid. The red vapor which distils over condenses to a red fuming liquid.

Chromium Trioxide, CrO$_3$ or $Cr {=\!=} O$ with O's —This substance is easiest obtained by treating a cold saturated solution of potassium dichromate with 1.5 volumes of concentrated sulphuric acid. The chromium trioxide separates on cooling in long dark-red crystals, which are sufficiently pure for many purposes. To prepare pure trioxide, chlorium hexfluoride is decomposed by water:

$$CrF_6 + 4H_2O = CrO_3 + H_2O + 6HF.$$

The red solution leaves on evaporation an amorphous red mass of the oxide, CrO_3.

Chromium trioxide melts at 193°, and at 250° is reduced to Cr_2O_3. It is one of the best oxidizing agents known. When alcohol is dropped upon it rapid combustion takes place. A solution of the trioxide in glacial acetic acid or sulphuric acid is often used to oxidize organic compounds, and a mixture of

potassium dichromate and sulphuric acid is much used for cleansing glass and porcelain in the laboratory.

Chromic Acid, H_2CrO_4 or $CrO_2{<}^{OH}_{OH}$.—This acid is supposed to have a constitution like that of sulphuric acid, because chromates are analogous to sulphates. It is obtained by the following process. Less water than is required to form H_2CrO_4 is added to chromium trioxide, the mixture heated to $100°$, the solution decanted, and cooled to $0°$, when small red crystals of chromic acid separate. These crystals, after drying over oil of vitriol, have the composition H_2CrO_4. The acid is very hygroscopic.

Potassium Chromate, K_2CrO_4 or $CrO_2{<}^{OK}_{OK}$.—This salt is obtained by adding potassium hydroxide to potassium dichromate:

$$\begin{matrix} CrO_2-OK \\ {>}O \\ CrO_2-OK \end{matrix} + 2KOH = 2CrO_2{<}^{OK}_{OK} + H_2O.$$
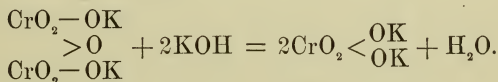
The solution on evaporation deposits at first red crystals of potassium dichromate, and afterwards yellow crystals of the chromate. Solutions of the chromate are decomposed by acids, even by carbonic acid, with formation of the dichromate. Potassium chromate is isomorphous with potassium sulphate. The salts $Na_2CrO_4 + 10H_2O$ and $Na_2SO_4 + 10H_2O$ are also isomorphous.

Lead Chromate, $PbCrO_4$ or $CrO_2{<}^{O}_{O}{>}Pb$.—This salt separates as a yellow precipitate when solutions of a lead salt and potassium dichromate are mixed. It is extensively used as a pigment known as chrome yellow. Lead chromate fuses at a red heat, and forms on cooling a compact brown mass, yielding a yellowish-brown powder. Above its melting point it

loses a portion of its oxygen. It is a valuable reagent, much used in the combustion of carbon compounds. Yellow lead chromate is converted by caustic alkalies into a chrome red, having the composition Pb_2CrO_5.

Dichromates are analogous in constitution to the disulphates. Dichromic acid,

$$\begin{array}{c} CrO_2-OH \\ >O \\ CrO_2-OH \end{array}$$

, has not been obtained,

but chrome sulphuric acid,

$$\begin{array}{c} CrO_2-OH \\ >O \\ SO_2-OH \end{array}$$

, is formed when CrO_3

is dissolved in H_2SO_4, just as disulphuric acid results from the union of SO_3 with H_2SO_4.

Potassium Dichromate, K_2CrO_{27} or

$$\begin{array}{c} CrO_2-OK \\ >O \\ CrO_2-OK \end{array}$$

.—This impor-

tant compound forms splendid red triclinic crystals, soluble in about ten parts of water at ordinary temperature, and more abundantly in boiling water. The salt fuses below a red heat, and at a higher temperature decomposes into oxygen, chromium sesquioxide, and potassium chromate. It is largely used in dyeing, and in the preparation of chromium compounds.

A film of gelatin and potassium dichromate darkens on exposure to light, the former becoming insoluble, and the latter being reduced to chromium sesquioxide. These changes are made use of in a photographic printing process.

Potassium dichromate is manufactured from chromic iron or chromite, $FeCr_2O_4$. A mixture of the ore, potassium carbonate, and lime is roasted; in the process oxygen is absorbed from the air, and potassium and calcium chromates are formed. The roasted mass is lixiviated with water, and potassium sulphate is added to the solution to precipitate the calcium as sulphate. To the hot concentrated solution sulphuric acid is added to convert the potassium chromate into dichromate, which

separates in crystals as the solution cools. Other dichromates are $(NH_4)_2Cr_2O_7$, $Na_2Cr_2O_7 + 2H_2O$, $Ag_2Cr_2O_7$, and $BaCr_2O_7 + 2H_2O$.

The following polychromates have also been prepared: potassium trichromate, $K_2Cr_3O_{10}$; tetrachromate, $K_2Cr_4O_{13}$; ammonia trichromate, $(NH_4)_2Cr_3O_{10}$; and hexchromate, $(NH_4)_2Cr_6O_{19}$. These compounds are viewed as similar in constitution to the dichromates, in that CrO_2 groups are joined by oxygen, thus:

$$CrO_2 <_{O}^{OK}$$
$$CrO_2 <_{O}^{O}$$
$$CrO_2 <_{OK}^{O}.$$
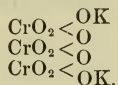
Perchromic Acid.—When hydrogen dioxide is added to a solution of chromic acid containing hydrochloric, sulphuric, or nitric acid, an indigo-blue solution results, which is supposed to contain perchromic acid. The color rapidly disappears, oxygen is evolved, and at the same time a chromic salt is formed. It has been found that for every molecule of potassium dichromate five molecules of hydrogen dioxide are required, and eight atoms of oxygen are set free. Based on these facts are the following equations:

$$K_2Cr_2O_7 + H_2O_2 + 2HCl = 2KCl + 2H_2O + Cr_2O_7.$$
$$Cr_2O_7 + 6HCl + 4H_2O_2 = 2CrCl_3 + 7H_2O + 8O.$$
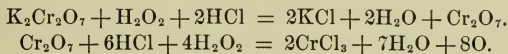
Cr_2O_7 is the anhydride of perchromic acid, $HCrO_4$, an analogue of $HClO_4$.

Perchromic acid is removed from its aqueous solution by ether. The ethereal solution of the acid is more permanent than the aqueous solution, losing oxygen, however, on evaporation and leaving chromium trioxide.

Potassium Chlorochromate, $CrO_2 <_{Cl}^{OK}$, is obtained by gently heating a mixture of 3 parts of potassium dichromate and 4 parts of strong hydrochloric acid and a little water:

$$K_2Cr_2O_7 + 2HCl = 2CrO_2 <_{Cl}^{OK} + H_2O.$$
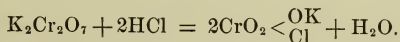
The salt crystallizes on cooling in reddish-yellow crystals. Potassium chlorochromate is decomposed by water with formation of potassium

dichromate and hydrochloric acid. It may, however, be recrystallized unchanged from aqueous hydrochloric acid. The dry salt is decomposed at 100° as follows.

$$4CrO_2 <^{OK}_{Cl} = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2.$$
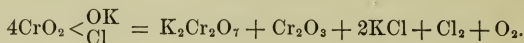
Chromyl Chloride or Chromium Oxychloride, $CrO_2 <^{Cl}_{Cl}$.—

To prepare this compound 10 parts of sodium chloride and 12 parts of potassium dichromate are fused together. The fused mass is broken into lumps and placed in a retort, and 30 parts of fuming sulphuric acid are added. The mixture is then heated, and the distillate is collected in a cooled receiver. Chromyl chloride is a blood-red liquid, boiling at 118°. Its observed gas density corresponds to the formula CrO_2Cl_2. Chromyl chloride is decomposed by water, with formation of chromic acid and hydrochloric acid.

Exp. 123.—Dissolve in a flask 20 grams of potassium dichromate in 150 cc. of water to which 20 cc. of sulphuric acid have been added. *a.* To a small portion of the solution add ammonia in excess, and note any changes. *b.* To the remainder of the solution add 10 cc. of alcohol, and warm gently. The irritating vapor given off is aldehyde, a product of the oxidation of alcohol. *c.* After the reaction appears to have ceased take a portion of *b* in a test-tube and add ammonia in excess. Note result and also the changes which alcohol has produced. Leave the remainder of *b* in a covered glass jar for a week or longer. Crystals of chrome alum will form.

Exp. 124.—*a.* To 100 cc. of a cold saturated solution of potassium dichromate add slowly and with constant stirring 150 cc. of strong sulphuric acid. The solution will deposit on cooling a portion of the chromium trioxide formed in the reaction. Pour off the mother-liquor. *b.* Transfer some of the trioxide to a porcelain dish, and add to it a few drops of alcohol. *c.* To a small portion of the trioxide in a test-tube add hydrochloric acid and warm the mixture. Chromium trichloride will be formed in the solution and chlorine evolved.

Exp. 125.—Mix 10 grams of pulverized potassium dichromate with 10 cc. of concentrated hydrochloric acid and 3 cc. of water. Warm

gently until the salt is dissolved. Crytals of potassium chlorochromate will form on cooling the solution.

Exp. 126.—Add a few drops of solution of potassium dichromate and also a few drops of hydrochloric acid to about 5 cc. of water in a test-tube and pour in sufficient ether to form a layer a centimeter in depth. Next add a little barium dioxide, which will react with the acid to form hydrogen dioxide. Close the tube with the thumb and agitate, but not violently. Note the result.

The reaction serves as a test for chromium, and also for hydrogen dioxide.

Molybdenum, Mo.

Atomic Weight, 96. *Density*, 8.6.

Molybdenum occurs sparingly in nature. Molybdenum trioxide, the compound used in making other compounds of molybdenum, is prepared from molybdenite, MoS_2, and wulfenite, the native molybdate of lead.

Metallic molybdenum is separated from its oxides or chlorides by hydrogen at high temperatures. When an oxide of molybdenum is intensely heated by the compound blowpipe in a carbon-lined crucible the metal obtained contains 4 to 5 per cent of carbon. It is very infusible, and harder than topaz. Molybdenum is permanent in air, and oxidizes only at high temperatures. It is not attacked by hydrochloric, hydrofluoric, or dilute sulphuric acid. It is oxidized by nitric acid, and is readily soluble in aqua regia.

Molybdenum alloys with lead, iron, copper, and gold, making them more brittle and less fusible.

The varying valence of molybdenum is shown by the compounds $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$, MoO_3, and MoS_4.

Molybdenum Pentachloride, $MoCl_5$, is obtained by gently heating molybdenum in pure chlorine. It is a black mass, which melts at 194° and boils at 268°. Its observed gas density corresponds to the formula $MoCl_5$. It may be sublimed in chlorine or carbon dioxide. Heated to 250° in hydrogen it is reduced to the trichloride, $MoCl_3$. This tri-

chloride, when heated in carbon dioxide, yields the dichloride and tetrachloride:

$$2MoCl_3 = MoCl_2 + MoCl_4.$$

The molybdenum chloride, $MoCl_6$, corresponding to MoO_3, has not been obtained.

Four oxides of molybdenum are known, viz.: MoO, Mo_2O_3, Mo_2, and MoO_3. The last is an acid anhydride; the others are basic oxides, whose corresponding chlorides have been mentioned.

Molybdenum Trioxide, MoO_3, is commonly called molybdic acid. It is a white powder which becomes yellow when heated. It fuses at a red heat in a closed vessel, and when heated in air sublimes at the temperature at which it melts. It is soluble in acids, and, if it has not been heated, is slightly soluble in water. The aqueous solution reacts acid with litmus.

Molybdenum trioxide is the anhydride of the acids $MoO_2(OH)_2$, $MoO(OH)_4$, and $Mo(OH)_6$. The first is perhaps formed when solutions of molybdates are decomposed by acids, the second separates as a yellow crust when a solution of ammonium molybdate in nitric acid stands a long time. The hexhydroxide perhaps exists in solution.

There are a number of polyacid molybdates which may be regarded as derived from salts of H_2MoO_4 by the addition of MoO_3, as illustrated by the following sodium compounds:

Sodium molybdate, . . .	$Na_2MoO_4 + 2H_2O$.
Sodium dimolybdate, . .	$Na_2MoO_4.MoO_3$.
Sodium trimolybdate, . .	$Na_2MoO_4.2MoO_3 + 7H_2O$.
Sodium tetramolybdate, . .	$Na_2MoO_4.3MoO_3 + 6H_2O$.
Sodium octomolybdate, . .	$Na_2MoO_4.7MoO_3 + 4H_2O$.
Sodium decamolybdate, . .	$Na_2MoO_4.9MoO_3 + 12H_2O$.

The constitution of these salts is probably similar to that of the polychromates.

Ammonium Molybdate, $(NH_4)_2MoO_4$, separates on adding alcohol to a solution of molybdenum trioxide in very strong ammonia. The ammonia solution of the trioxide leaves on evaporation crystals of the salt $(NH_4)_6Mo_7O_{24} + 4H_2O$.

Phosphomolybdic Acid.—Phosphoric and molybdic acids unite in different proportions to form compound acids. The one richest in molyb-

dic acid is obtained by evaporating an aqueous solution of phosphoric and molybdic acids. Yellow crystals separate, having the composition $2H_3PO_4.24MoO_3 + 58H_2O$, which at 140° lose water of crystallization.

Ammonium Phosphomolybdate forms a yellow precipitate when orthophosphoric acid or an orthophosphate is added to a large excess of a solution of ammonium molybdate in nitric acid, known as molybdic solution. Some investigators have found such a preparation to have the composition $2[(NH_4)_2PO_4].22MoO_3 + 12H_2O$. Other results have been obtained which correspond to 20 and 24 MoO_3 to 2 atoms of phosphorus. Ammonium phosphomolybdate is slightly soluble in water, and is insoluble in molybdic solution. It is readily soluble in ammonia Molybdic solution is an indispensable reagent for the separation of phosphoric acid.

Exp. 127.—Add one drop of solution of common sodium phosphate to a few cubic centimeters of molybdic solution. An excess of phosphate will prevent the formation of a precipitate.

Tungsten (Wolfram), W.

Atomic Weight, 184.   *Density*, 19.1.

Tungsten is not a very abundant element. Wolframite, an iron and manganese tungstate, is the common ore of tungsten. Scheelite, $CaWO_4$, and stolzite, $PbWO_4$, are important tungsten minerals.

Metallic tungsten is prepared by reducing the oxide with carbon or hydrogen. The metallic powder thus obtained has a bright-gray lustre, and is sufficiently hard to scratch glass. Tungsten is more infusible than molybdenum, and has only been fused in an atmosphere of nitrogen by means of a powerful galvanic current. The metal in form of powder is not changed by moist or dry air, and at a red heat burns in air to the trioxide. Hot nitric, hydrochloric, and sulphuric acid slowly, and aqua regia quickly, convert the metal into trioxide. A boiling solution of potassium hydroxide attacks the metal, potassium tungstate being formed and hydrogen evolved. Tungsten is said to improve the quality of steel, but little use has as yet been made of tungsten steel.

The varying valence of tungsten is exhibited by the chlorides, WCl_2, WCl_4, WCl_5, and WCl_6.

Tungsten Hexchloride, WCl_6, is formed by the direct union of its elements. It melts at 275° and boils at 346°. Its gas density at temperatures near its boiling point has been found to correspond to WCl_6. At higher temperatures it dissociates into free chlorine and the following compound:

Tungsten Pentachloride, WCl_5, is obtained by repeated distillation of the hexchloride in an atmosphere of hydrogen. It melts at 248° and boils at 275°.6, and its gas density accords with WCl_5.

Tungsten Tetrachloride, WCl_4, forms a non-volatile residue when the higher chlorides are repeatedly distilled in hydrogen. It is decomposed by heat into the volatile pentachloride and tungsten dichloride, which remains as an amorphous gray powder.

There are two oxides of tungsten, WO_2 and WO_3. The first is a feeble base and the last is an acid anhydride.

Tungsten Dioxide, WO_2, is obtained as a brown powder when the trioxide is reduced by hydrogen at a dull-red heat. By acting upon the trioxide with zinc and dilute hydrochloric acid, copper-red crystals of the dioxide are formed. It dissolves in warm hydrochloric and sulphuric acid to a purple-colored solution.

Tungsten Trioxide, WO_3, occurs native. It is obtained by igniting tungstic acid, and is commonly prepared from wolframite. The pulverized mineral is digested with hydrochloric acid, and the solution containing iron and manganese chlorides poured off. The yellow product is dissolved in ammonia to separate any undecomposed mineral, and the solution is evaporated to dryness. This residue on ignition is converted into the trioxide, a bright yellow powder. At 250° in presence of hydrogen it is converted into a blue compound, having the composition $2WO_3 + WO_2$. Tungsten trioxide is insoluble in water and acid, but dissolves in ammonia, and alkali hydroxides and carbonates with formation of tungstates.

Tungsten trioxide is the anhydride of the acids $WO_2(OH)_2$, $WO(OH)_4$, and $W(OH)_6$.

Dimetatungstic Acid, $WO_2(OH)_2$, separates as a yellow powder when an alkali tungstate is treated with an excess of hot acid. It is in-

soluble in water, but is dissolved by hydrofluoric acid and an excess of concentrated hydrochloric acid. The sodium salt, $WO_2(ONa)_2$, is prepared by fusing a mixture of tungsten trioxide and sodium carbonate. It crystallizes with two molecules of water.
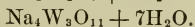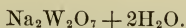
Monometatungstic Acid, $WO(OH)_4$, forms a white precipitate when a mineral acid is added to a cold dilute solution of an alkali tungstate. It is somewhat soluble in water, and reddens litmus. It changes on standing, more rapidly when heated, to the yellow dimetatungstic acid.

Orthotungstic Acid, $W(OH)_6$, is perhaps formed when a solution of sodium tungstate is treated with sufficient hydrochloric acid to form chloride with all the sodium. After dialyzing the solution for removal of the sodium chloride the solution yields on evaporation a gummy mass which may be heated to 200° without becoming insoluble in water.

Tetratungstic Acid, $H_2W_4O_{13}$.—The constitution of this acid is supposed to be analogous to that of the polychromic and molybdic acids. It is termed metatungstic acid by some writers. It is obtained by adding dilute sulphuric acid to a warm concentrated solution of barium tetratungstate. The solution deposits on evaporation in vacuum small crystals of $H_2W_4O_{13} + 7H_2O$, which at 100° lose their seven molecules of water. The solution of tetratungstic acid is strongly acid. It may be boiled without change and evaporated on a water-bath to a syrup, but on further heating suddenly changes to the common yellow tungstic acid.

Sodium Tetratungstate, $Na_2W_4O_{13} + 10H_2O$, is prepared by boiling the salt $Na_2WO_4 + 2H_2O$ with tungsten trioxide. It is very soluble in water.

In addition to the sodium salts already described the following have been obtained:

$$Na_2W_2O_7 + 2H_2O.$$
$$Na_4W_3O_{11} + 7H_2O.$$
$$Na_4W_5O_{17} + 11H_2O.$$
$$Na_6W_7O_{24} + 16H_2O.$$
$$Na_6W_7O_{24} + 21H_2O.$$
$$Na_{10}W_{12}O_{41} + 21 \text{ or } 25 \text{ or } 28 \text{ } H_2O.$$
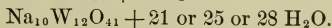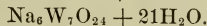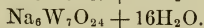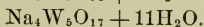
These sodium polytungstates may be viewed as having a constitution analogous to the polysulphates and polychromates, but with this difference, namely, that some of the salts contain more than two atoms of

basic metal. These latter are formed from Na_2WO_4 and WO_3 in different proportions. The salt $Na_4W_3O_{11}$ may be graphically represented thus :

$$\begin{matrix} \left.\begin{matrix} NaO \\ NaO \end{matrix}\right> WO \\ WO_2 \\ \left.\begin{matrix} NaO \\ NaO \end{matrix}\right> WO \end{matrix} \begin{matrix} >O \\ >O \end{matrix} \quad\quad >O$$
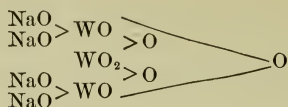
The salt $Na_{10}W_{12}O_{41}$ is manufactured by roasting wolframite with soda ash, and exhausting the fused mass with hot water. The boiling solution is nearly neutralized by hydrochloric acid and left to crystallize at common temperatures. This salt is used to render fabrics uninflammable.

Barium Tetratungstate, $BaW_4O_{13} + 9H_2O$, separates in crystals when hot saturated solutions of sodium tetratungstate and barium chloride are mixed.

Tungsten Sodium Bronze.—When a sodium polytungstate is fused with tin and the product successively treated with water, hydrochloric acid, and sodium hydroxide, fine golden-yellow cubes of tungsten sodium bronze remain. The compound is used for bronze powders.

Tungstic acid forms very complex compounds with phosphoric acid, analogous to the phosphomolybdates.

Uranium, U.

Atomic Weight, 239.   *Density,* 18.7.

Uranium is mostly obtained from the mineral uranite or pitch blende, which consists of U_3O_8 and impurities. It also occurs in a few other minerals. The metal is best prepared by heating uranium tetrachloride with sodium and sodium chloride in an iron crucible closed with a screw cap. At a red heat it separates as a grayish-black powder, which fuses at a white heat to globules. The fused uranium is silver white, somewhat malleable, and not quite as hard as steel. It gradually corrodes in air, becoming first steel-blue, and finally black. Uranium powder ignites in air or oxygen at 150° to 170°, and burns brilliantly.

The atomic weight of uranium was for a long time regarded as 120. The close analogy of its compounds with those of molybdenum and tungsten has, however, recently led to the adoption of double this number as the true atomic weight. Further, the determination of the specific heat of the metal and the gas densities of some of its compounds confirms this view

The different classes of compounds which uranium is capable of forming are illustrated by the following: UCl_3, UCl_4, UCl_5, UO_2, U_2O_5, UO_3, and the little understood UO_4, $UO_4 + 2H_2O$, $K_4UO_8 + 10H_2O$.

Uranium Trichloride, UCl_3, results when the tetrachloride is heated to near the temperature of volatilization in hydrogen:

$$UCl_4 + H = UCl_3 + HCl.$$
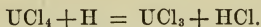
Uranium Tetrachloride, UCl_4, is formed by the direct union of its elements, and is prepared by passing dry chlorine over a hot mixture of uranium oxide and charcoal. Its observed gas density is 192.9, theory requiring 185.2 for UCl_4.

Uranium Pentachloride, UCl_5, is formed by the direct addition of chlorine to the tetrachloride. The pentachloride begins to dissociate at 120° into the tetrachloride and chlorine, and at 235° the dissociation is complete.

The oxides of uranium are $UO(?)$, $U_2O_3(?)$, UO_2, UO_3, UO_4, U_2O_5, and U_3O_8.

Uranium Dioxide or Uranous Oxide, UO_2, is obtained by heating a higher oxide in hydrogen. It was formerly regarded as metallic uranium. It is a basic oxide, forming green salts. The sulphate has the composition $U(SO_4)_2 + 8H_2O$.

Uranium Trioxide or Uranic Oxide, UO_3, is formed when uranyl nitrate is heated to 250°. Towards acids it is basic, and forms salts containing the bivalent radical uranyl, UO_2. Fused with alkali carbonates it forms uranates. The uranyl salts are yellow. Glass colored yellow by them is remarkable for its fluorescence.

Uranic Acid or Uranyl Hydroxide, $UO_2(OH)_2$.—This hydroxide does not separate on addition of an alkali hydroxide to a solution of a uranyl salt owing to formation of a uranate. When a solution of uranyl nitrate in absolute alcohol is evaporated a violent reaction occurs, and a mass re-

mains, which, after treatment with water, leaves a compound of the composition H_2UO_4.

Uranyl Chloride, $UO_2=Cl_2$, is formed by the direct union of uranous oxide and chlorine at a red heat. It is soluble in water without decomposition.

Uranyl Nitrate, $\dfrac{NO_2-O}{NO_2-O}>UO_2 + 6H_2O$.—This salt is formed when any oxide of uranium is dissolved in nitric acid. It is soluble in half its weight of water.

Uranates.—Potassium diuranate, $K_2U_2O_7$, and other diuranates are analogous to the dichromates. More complex polyuranates are known.

Uranium Pentoxide, U_2O_5, is formed when any one of the oxides is intensely ignited in air. It is a black powder used as a black pigment on porcelain.

Green Oxide of Uranium, U_3O_8, is a dark-green powder formed when either UO_2 or UO_3 is ignited in air, or better in oxygen.

Peruranates.—Hydrogen dioxide produces in a solution of uranyl nitrate a yellowish-white precipitate, having the composition $UO_4 + 2H_2O$, which dissolves in hydrochloric acid with evolution of chlorine. On adding uranyl nitrate to a large excess of sulphuric acid containing hydrogen dioxide there separates after some time a colorless crystalline powder which is UO_4. Alcohol throws down from a solution containing uranyl nitrate, potassium hydroxide, and hydrogen dioxide, a reddish yellow precipitate of $K_4UO_8 + 10H_2O$, which loses oxygen and absorbs carbon dioxide on exposure to air.

Summary of the Sixth Group.

The sixth group comprises two well-defined sub-groups, one containing the non-metals oxygen, sulphur, selenium, and tellurium, and the other the metals chromium, molybdenum, tungsten, and uranium. Oxygen and sulphur are non-metallic in all respects, while selenium and tellurium possess some metallic properties. All the non-metals of the group form acids with hydrogen and oxygen, and in no case bases; they

also form hydrides, but the metals of the group do not combine with hydrogen. The oxygen halide OCl_2 is analogous in formula, but not in properties, to the dichlorides of other elements of the group, and there are no analogues of O_2Cl and O_5I_2. The following are halides of this group, oxygen excepted:

Sulphur, .	. S_2Cl_2	SCl_2	——	SCl_4	——	SI_6
Selenium,	. Se_2Cl_2	——	——	$SeCl_4$	——	——
Tellurium,	. . .	$TeCl_2$	——	$TeCl_4$	——	——
Chromium,	. . .	$CrCl_2$	$CrCl_3$	——	——	CrF_6
Molybdenum,	. .	$MoCl_2$	$MoCl_3$	$MoCl_4$	$MoCl_5$	——
Tungsten,	. . .	WCl_2	——	WCl_4	WCl_5	WCl_6
Uranium,	. . . .	——	UCl_3	UCl_4	UCl_5	——

The halides of sulphur, selenium, and tellurium are not of the nature of halide salts, as is evident from their decomposition by water with formation of oxy-acids, thus:

$$2S_2Cl_2 + 3H_2O = H_2SO_3 + 4HCl + 3S.$$
$$TeCl_4 + 3H_2O = H_2TeO_3 + 4HCl.$$
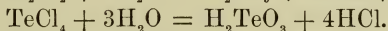
Chromium, molybdenum, tungsten, and uranium are basic in the lower and acidic in the higher halides. Chromium trichloride, for example, is changed by potassium hydroxide to $Cr(OH)_3$, a base which forms salts with acids. The hexfluoride, on the contrary, reacts with water to form chromic acid, thus:

$$CrF_6 + 4H_2O = H_2CrO_4 + 6HF.$$
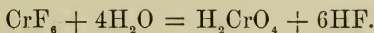
OXIDES.

Sulphur, ...	S_2O_3	SO_2	SO_3
Selenium, ...	——	SeO_2	——
Tellurium, ...	——	TeO_2	TeO_3
Chromium, ...	Cr_2O_3	——	CrO_3
Molybdenum, ...	Mo_2O_3	MoO_2	MoO_3
Tungsten, ...	——	WO_2	WO_3
Uranium, ...	——	UO_2	UO_3

HYDROXIDES.

Sulphur,	——	——	$SO(OH)_2$	$SO_2(OH)_2$
Selenium,	——	——	$SeO(OH)_2$	$SeO_2(OH)_2$
Tellurium,	——	——	$TeO(OH)_2$	$TeO_2(OH)_2$
Chromium,	$Cr(OH)_2$	$Cr(OH)_3$	——	$CrO_2(OH)_2$
Molybdenum,	——	——	——	$MoO_2(OH)_2$
Tungsten,	——	——	——	$WO_2(OH)_2$
Uranium,	——	——	——	$UO_2(OH)_2$

The hydroxides of sulphur, selenium, and tellurium are acids. The hydroxides $Cr(OH)_2$ and $Cr(OH)_3$ are bases, while $CrO_2(OH)_2$ is an acid. The salts of molybdic acid, $MoO_2(OH)_2$, and tungstic acid, $WO_2(OH)_2$, and the complex molybdates and tungstates, are more stable than the compounds in which molybdenum and tungsten are basic. The radical uranyl, UO_2, is acidic or basic in character according as it is united to basic or acidic radicals, as for example in potassium uranate, $\begin{matrix} UO_2 \diagup O\text{-}K \\ UO_2 \diagup O \diagdown O\text{-}K \end{matrix}$, and uranyl sulphate, $SO_2 {<}^O_O{>} UO_2$.

Oxygen, with the lowest atomic weight of any member of the sixth group, stands apart in most properties from the other elements of this decidedly acidic group. Since the acidic character of the hydroxides of the group is closely related to the number of atoms of oxygen contained in them, it appears that oxygen is acidic in character, and is, as its name indicates, an acid former. For example, the lower hydroxides of chromium are not acids, but $CrO_2(OH)_2$ is, like $SO_2(OH)_2$, a strong acid. Moreover, the basic oxides and hydroxides, as a rule, contain fewer atoms of oxygen than oxygen acids.

The properties which an element exhibits in a compound depend upon the relations existing between all the elements of the compound. Thus oxygen may be acidic in acids and not in bases. In acids containing the same negative element the difference between them depends upon their content of oxygen. For example, sulphurous and sulphuric acids differ by one atom of oxygen.

THE SECOND GROUP.

THE elements of this group are bivalent basic metals. Beryllium, with the lowest atomic weight, stands apart from the other members, and in some properties resembles aluminum of the third group. Mercury, with the highest atomic weight in the group, also stands apart, and in mercurous compounds resembles in its univalent character the elements of the first group.

Calcium, strontium, and barium are closely related, and constitute the well-defined sub-group known as the alkali-earth metals. Zinc, cadmium, and mercury are heavy metals, which present little similarity to the other members of the group. Magnesium is intermediate in properties between the alkali-earth metals and zinc.

Beryllium, Be.

Atomic Weight, 9. *Density,* 2.1.

Beryllium is found in a number of minerals, of which the most familiar is beryl, a silicate of aluminum and beryllium. Emerald and aquamarine are varieties of beryl, which are valued as gems.

Metallic beryllium is obtained by heating the chloride with sodium. It is a malleable white metal, more fusible than silver. It does not decompose water at a red heat.

Beryllium Chloride, $BeCl_2$, is prepared by heating the oxide mixed with carbon in a current of chlorine, and also by heating the metal in dry hydrochloric acid gas. The gas density of it has been found to be 40; theory requires 39.9 for $BeCl_2$.

Beryllium Oxide, BeO, is a white powder obtained by igniting the hydroxide. It is insoluble in water, and after intense ignition dissolves slowly in acids.

Beryllium Hydroxide, Be(OH)$_2$.—Ammonia produces in a solution of a beryllium salt a gelatinous precipitate which, on drying at 100°, has the composition Be(OH)$_2$. It is soluble in acids, caustic alkalies, and ammonium carbonate.

Beryllium Sulphate, BeSO$_4$, crystallizes with four and seven molecules of water.

Alkali-Earth Metals.

Calcium: Atomic Weight, 40. Strontium: Atomic Weight, 87.5. Barium: Atomic Weight, 137.

The oxides of these metals are called alkali-earths, because in many of their properties they stand intermediate between the alkalies and the so-called earthy oxides of aluminum and iron. Their hydroxides in basic qualities rank next to the alkalies, and are sufficiently soluble in water to exhibit alkaline taste and deportment with test papers.

These metals in their analogous compounds show a gradation in properties related to their difference in atomic weights. The solubility of the hydroxides increases from calcium to barium, and the solubility of the chlorides and sulphates diminishes in the same order. Calcium hydroxide is changed to oxide at a red heat, and barium hydroxide loses water only on intense ignition. In no case has the gas density of a compound of the alkali-earth metals been determined: hence the received molecular formulas of their compounds rest on analogy. One atom of each of these metals replaces two of hydrogen, and they are therefore regarded as dyads. Their oxides, hydroxides, and chlorides are illustrated by the formulas $Ca = O$, $Sr < {OH \atop OH}$, $Ba < {Cl \atop Cl}$.

Calcium, Ca.

Atomic Weight, 40.   *Density,* 1.58.

Calcium is a very common element, forming about one sixteenth of the crust of the earth. It occurs abundantly in limestones and many other rocks, and in the bones and shells of animals, and is an essential ingredient of soils. Sea, river, and spring waters contain salts of calcium.

Metallic calcium was first isolated by Davy, in 1808, by subjecting its oxide mixed with mercury to a powerful galvanic current. It is more easily prepared by the electrolysis of its chloride, and is also obtained by decomposing calcium iodide with sodium at a high temperature in a closed vessel. Calcium is a yellow metal, malleable and tenacious, and harder than tin. It oxidizes readily in moist air, and decomposes water rapidly with evolution of hydrogen.

Calcium Chloride, $CaCl_2$ or $Ca < {Cl \atop Cl}$, is formed when calcium oxide, hydroxide, or carbonate is dissolved in hydrochloric acid.

Exp. 128.—*a.* Dilute 50 cc. of concentrated hydrochloric acid with twice its bulk of water, and add crushed marble in excess. When the escape of carbon dioxide has nearly ceased, pour in a little chlorine water to oxidize iron compounds which may be present, and heat to boiling, then add milk of lime to alkaline reaction, and boil a few minutes. Filter from the excess of lime which carries with it any iron, aluminum, magnesium, silicon, or phosphorus that may have been present in the solution. Make the filtrate acid by a few drops of pure hydrochloric acid, and evaporate in a porcelain dish to a syrupy consistence.

b. Pour part of the liquid into a test-tube, and leave to cool and crystallize. *c.* Evaporate the remainder to dryness, and heat the residue moderately for some time to drive off all the water.

d Leave some of the dry salt exposed, and note that it soon deliquesces unless the air is very dry.

Anhydrous calcium chloride made as described in the above experiment is an opaque porous mass which is valuable for

drying gases. It melts at a red heat, and solidifies on cooling to a crystalline mass. The fused salt is also used as a drying agent, being serviceable for removing water from various organic liquids.

Calcium chloride separates on cooling a concentrated solution in crystals containing six molecules of water. A mixture of crushed crystals and snow lowers the temperature sufficiently to freeze mercury. Both the hydrous and anhydrous salt deliquesce in moist air, and are very soluble in water.

Slaked lime dissolves in a boiling solution of calcium chloride, and the solution filtered hot deposits on cooling crystals of calcium hydroxy-chloride, $Ca<\overset{OH}{\underset{}{}}$ $Ca<\overset{O}{\underset{Cl}{}} + 7H_2O$. This compound is decomposed by water into $CaCl_2$ and $Ca(OH)_2$.

Calcium Bromide, $CaBr_2$, and **Calcium Iodide, CaI_2,** are soluble deliquescent salts.

Calcium Fluoride, CaF_2 or $Ca<\overset{F}{\underset{F}{}}$, occurs as fluor spar (fluorite), and is the most abundant compound of fluorine. It is used as a flux, and in the manufacture of hydrofluoric acid. Unlike the other halides of calcium, it is insoluble in water.

Calcium Oxide, CaO or $Ca=O$, commonly known as lime or quick-lime, is made by heating to bright redness calcium carbonate (limestone, marble, or oyster-shells) in lime-kilns. In the large kilns, arranged for continuous burning, limestone or shells and fuel are put into the top from time to time, and lime removed from the base. The carbonate is decomposed by heat into calcium oxide and carbon dioxide, thus :

$$CO<\overset{O}{\underset{O}{}}>Ca = Ca=O + C\overset{O}{\underset{O}{\lessgtr}}.$$
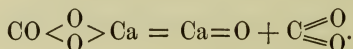
The decomposition of the carbonate is facilitated by the presence of steam or gases which dilute the carbon dioxide,

since lime heated to redness in pure carbon dioxide absorbs the gas with reproduction of the carbonate. Pure lime is white, amorphous, and infusible. It slowly absorbs moisture and carbon dioxide from the air, and after a time falls to a powder of air-slaked lime.

Calcium Hydroxide, Ca(OH)$_2$ or $Ca{<}^{OH}_{OH}$, is commonly known as slaked lime. It is formed more or less readily when quick-lime is drenched with water :

$$Ca{=}O + H{-}O{-}H = Ca{<}^{OH}_{OH}.$$
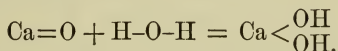
Impure lime, especially that made from limestone containing clay, slakes very slowly.

Exp. 129.—*a.* Place in an iron or wooden vessel a kilo or more of good lime, and add half its weight of water. After some minutes the water is taken up by the lime, which becomes hot, and falls to a dry white powder. *b.* Heat a portion of the dry hydroxide to redness in a small glass tube, and observe that water is given off. *c.* Slake a lump of lime in a considerable quantity of hot water. The product is milk of lime.

The heat evolved in the slaking of lime is a result of the chemical union of lime and water, and also the passage of the latter into the solid state. When large quantities of lime are rapidly slaked sufficient heat is produced to char wood.

Calcium hydroxide is sparingly soluble in cold water, and, contrary to the general rule, is less soluble in hot water. One part of the hydroxide requires for its solution about 700 parts of ice-cold water, and twice as much boiling water.

Exp. 130.—*a.* Add some milk of lime to water in a bottle, and filter the solution obtained; or cork the bottle and allow the mixture to stand until the lime has subsided, when the clear lime water may be siphoned off. *b.* Heat saturated lime water to boiling. *c.* Taste lime water, and note its reaction with test-papers.

Lime water readily absorbs carbon dioxide from the air, with formation of a film or precipitate of calcium carbonate. It is used in medicine as a mild alkali. Lime is the cheapest base, and hence finds extensive application in the chemical industry. It is used in preparing caustic potash and soda from their carbonates, for liberating ammonia from its salts, for removing carbon dioxide and sulphur from illuminating gas, and for neutralizing acids in various processes. But the largest consumption of lime is for making the mortar used in ordinary brick and stone work, and for plastering walls. Mortar is a plastic mixture of slaked lime, sand, and water. The pasty slaked lime adheres strongly to the surfaces of the grains of sand and building materials; the admixed water in the mortar dries out ; then the mortar becomes tougher owing to the gradual absorption of carbon dioxide with formation of calcium carbonate and liberation of water, according to the equation—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
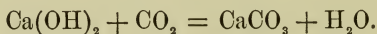
Hence the prolonged dampness of newly-plastered walls.

Calcium Dioxide, CaO_2.—When hydrogen dioxide is added in excess to lime water, $CaO_2 + 8H_2O$ is precipitated in small crystals, which effloresce in the air, and become anhydrous at $130°$. On ignition CaO_2 loses half its oxygen.

Calcium Hypochlorite, $Ca(OCl)_2$, is formed when hypochlorous acid is neutralized with lime, and also together with calcium chloride by acting on milk of lime with chlorine, thus :

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$
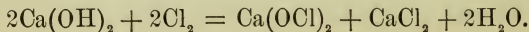
Bleaching Powder or Chloride of Lime.—This well-known substance is extensively manufactured by exposing slaked lime to chlorine. The gas is absorbed, and the product is a dry white powder, which has a chlorine-like odor, due to the

escape of hypochlorous acid, which is set free by the action of the carbon dioxide of the air.

Various views have been held regarding the constitution of bleaching powder. Formerly it was regarded as a mixture of calcium hypochlorite, calcium chloride, and unchanged slaked lime. Odling has represented the portion soluble in water by the formula $Ca{<}^{Cl}_{OCl}$, while others have viewed bleaching powder as a mixture of basic calcium hypochlorite and calcium chloride, formed thus :

$$3Ca(OH)_2 + 2Cl_2 = 2Ca{<}^{OH}_{OCl} + CaCl_2 + 2H_2O.$$
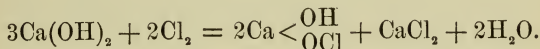
Schlaeppi assigns to the bleaching substance the formula $2CaOCl_2 . H_2O$.

Bleaching powder, treated with cold water, leaves a residue of slaked lime, and the solution contains calcium hypochlorite and calcium chloride. Moderately dilute sulphuric and hydrochloric acids liberate chlorine :

$$CaCl_2 + Ca(OCl)_2 + 4HCl = 2Cl_2 + 2CaCl_2 + 2H_2O.$$
$$CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2Cl_2 + 2CaSO_4 + 2H_2O.$$
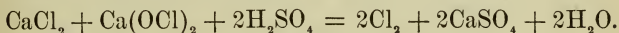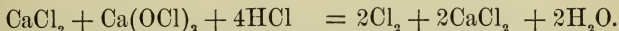
Bleaching powder gives off the oxygen of the hypochlorite when heated to redness. When dilute solutions are boiled calcium chlorate is formed. Bleaching powder is largely used to bleach cotton fabrics and paper, and as a deodorizer and disinfectant.

Exp. 131.—Shake together a teaspoonful of bleaching powder and about 200 cc. of water. Wet thoroughly some bits of calico in the solution, then put them into very dilute hydrochloric acid, and repeat the treatment with the bleaching powder solution and acid several times. Also try bleaching printed paper, ink and pencil marks.

Exp. 132.—To a spoonful of bleaching powder in a tall cylinder add sulphuric acid diluted with its bulk of water.

Calcium Sulphate, CaSO$_4$ or $SO_2 <^O_O> Ca$, is abundant in
nature.   It occurs free from water as the mineral anhydrite
and combined with water as gypsum, $CaSO_4 + 2H_2O$, of which
the translucent massive variety is alabaster, and the beauti-
fully transparent crystallized forms are selenite.   Hydrous
calcium sulphate dissolves in 415 parts of water at 0°, in 368
parts at 38°, and in 451 parts at 99°.   It is commonly found
together with calcium carbonate in natural waters, and adds
to their "hardness" and to the formation of boiler-scale.
When gypsum is heated to 100° or 110° it readily loses most
of its water, but a temperature of 200° to 250° is required to
render it anhydrous.

Calcined gypsum, commonly known as plaster of Paris, re-
covers water of crystallization when mixed with water, and
hardens to a compact mass, expanding somewhat at the same
time.   It is used for making casts, and mixed with slaked lime
and sand for hard-finishing walls.   Plaster of Paris calcined
at a low temperature sets more quickly than when strongly
heated.

Exp. **133.**—Mix plaster of Paris with water to the consistency of thick
cream.   Place a coin, slightly greased, on paper, and pour the plaster
over it.   Rub the coin with the finger to displace air bubbles, and leave
the plaster undisturbed until hard.

Strontium, Sr.

Atomic Weight, 87.5.   *Density*, 2.5.

The more common strontium minerals are the carbonate or
strontianite, $SrCO_3$, and the sulphate or celestite, $SrSO_4$.   Many
limestones contain traces of strontium.   Metallic strontium is
obtained by the electrolysis of the fused chloride.   It has a

yellow color, and is harder than calcium or lead. It oxidizes in the air, and decomposes water rapidly. The strontium salts color the flame a brilliant crimson.

Strontium Chloride, $SrCl_2 + 6H_2O$, is a deliquescent salt, somewhat soluble in alcohol.

Strontium Oxide, SrO, is obtained by igniting the nitrate. With water it forms **strontium hydroxide, $Sr(OH)_2$,** which is more soluble than calcium hydroxide, and which crystallizes with eight molecules of water. The hydroxide is converted into oxide only on intense ignition.

Strontium Dioxide, SrO_2, and its hydrate, $SrO_2 + 8H_2O$, have been prepared.

Strontium Sulphate, $SrSO_4$, separates as a heavy white powder on addition of sulphuric acid or soluble sulphate to a solution of a strontium salt. It is more soluble in water than barium sulphate, and less than calcium sulphate.

Barium, Ba.

Atomic Weight, 137. *Density,* 4.

Barium is more abundant than strontium, and the chief source of it is barite or heavy spar, $BaSO_4$. It occurs in many other minerals. Metallic barium tarnishes on exposure, and decomposes water. It is separated by electrolyzing the fused chloride. The soluble barium compounds are poisonous. The volatile barium compounds impart a yellowish-green color to a non-luminous flame.

Barium Chloride, $BaCl_2$ or **$Ba{<}{Cl \atop Cl}$,** is the cheapest soluble salt of barium, and is therefore extensively used in preparing

other barium compounds.   It is made by treating either the
sulphide or the native carbonate with hydrochloric acid.   It
crystallizes from solution as $BaCl_2 + 2H_2O$ in rhombic crystals,
which are permanent in the air.

Barium Oxide, BaO, is obtained by igniting the nitrate or
iodate as a grayish-white substance.   It combines energetically
with water to form the hydroxide.

Exp. 134.—Heat barium nitrate in a porcelain crucible gently at first
and finally over the blast lamp. When cool, drop upon it a little water.
The mass will glow. A strongly alkaline solution of the hydroxide will
be obtained on dissolving the oxide in hot water.

Barium Hydroxide, $Ba(OH)_2$ or $Ba{<}{OH \atop OH}$, is manufactured
from heavy spar by a somewhat complicated process.   It
crystallizes from water as $Ba(OH)_2 + 8H_2O$.   It loses seven
molecules of water in vacuum over sulphuric acid; at a red
heat the eighth molecule is driven off, and $Ba(OH)_2$ remains
as an oily liquid, which solidifies on cooling.   Crystals of
$Ba(OH)_2 + 8H_2O$ dissolve in 3 parts of boiling water and
in 20 parts at 15°.   Barium hydroxide is a strong base much
used in chemical analysis, and is known as caustic baryta, and
its solution as baryta water.   It absorbs carbon dioxide from
the air with formation of barium carbonate.

Barium Dioxide, BaO_2, is formed when oxygen or dry air free
from carbon dioxide is passed over glowing barium oxide or
hydroxide.   The conversion is not complete, as the product
always contains unchanged oxide.   On adding a solution of
barium hydroxide to hydrogen dioxide, the hydrated dioxide,
$BaO_2 + 8H_2O$, separates in crystals.   These, on heating to
130°, are changed into a white powder of pure anhydrous
barium dioxide.   The dioxide is also formed when a mixture
of barium oxide or hydroxide and potassium chlorate is heated
to dull redness.   The potassium chloride formed is removed
by water, the dioxide then remaining as a hydrate.

Exp. 135.—Stir commercial barium dioxide in water and slowly add hydrochloric acid until nearly all is dissolved. The solution contains hydrogen dioxide and the impurities of the barium dioxide. A strong solution of barium hydroxide is added, little by little, to precipitate the silica and metallic oxides, until a little hydrated barium dioxide is formed. The solution is filtered, and barium hydroxide is added as long as the hydrated dioxide separates. The crystals may be washed by decantation, and kept without drying for use in preparing a pure solution of hydrogen dioxide.

Barium Sulphate, $BaSO_4$ or $SO_2{<}{\overset{O}{\underset{O}{}}}{>}Ba$, falls as a heavy white powder on addition of sulphuric acid or a soluble sulphate to a solution of a barium salt. It constitutes the mineral barite or heavy spar, which occurs in large transparent or translucent colorless crystals. It is very insoluble, one part of the salt requiring 400,000 parts of water for its solution. Ground heavy spar is largely used to adulterate white lead, to which it is inferior as a pigment. The artificial sulphate has better covering properties, and is also used in paints.

Barium Iodate, $Ba(IO_3)_2 + 2H_2O$, separates when iodine is added to a solution of barium hydroxide. It is soluble in about 600 parts of boiling water and in 3000 parts of cold water.

Barium Monosulphide, BaS, is obtained pure by passing hydrogen sulphide over hot baryta. The crude sulphide is manufactured by roasting ground heavy spar mixed with coal-dust. Barium sulphide is decomposed by water, thus:

$$2BaS + 2H_2O = Ba(HS)_2 + Ba(OH)_2.$$
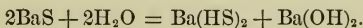
Barium Hydrosulphide, $Ba(HS)_2$, is made by saturating a solution of barium hydroxide with hydrogen sulphide. The solution, when evaporated out of contact with air, yields colorless crystals. When a solution of the hydrosulphide is boiled with sulphur, a yellow, caustic, and alkaline solution of BaS_5 is obtained, which yields on evaporation in vacuum free sulphur, and red crystals of the tetrasulphide, BaS_4.

Magnesium, Mg.

Atomic Weight, 24.4.　*Density,* 1.75.

Magnesium is not as abundant as calcium, with which it is commonly associated. It is found in plants, milk, blood and bones, and in sea and river waters. Many mineral springs owe their saline character to magnesium sulphate and chloride. Magnesium silicates are common in rocks. Serpentine is a hydrous silicate, and talc is an anhydrous silicate of magnesium. Dolomite, composed of magnesium carbonate and calcium carbonate, often occurs in rock masses. Magnesium is not found free in nature, although the metal is not altered by air and moisture, as are the metals of the alkalies and alkali-earths.

The metal may be separated by electrolysis, or better by heating its chloride with sodium.

Magnesium is almost as white as silver, is malleable, melts between 700° and 800°, and distils at a higher temperature. Distillation is a means of purifying the metal. The air at ordinary temperatures acts but slightly on the metal, since the oxide and hydroxide formed adhere firmly, thus protecting it from further corrosion. Magnesium, in the form of wire, ribbon, and filings, burns with a brilliant, dazzling white light, remarkable for its actinic rays. A mixture of chlorine and hydrogen may be exploded by this light. Magnesium lamps are constructed for burning magnesium ribbon, and are used for illumination in photography when sunlight is not available. The metal when pure does not decompose water at 100°. It dissolves with evolution of hydrogen in dilute acids, even carbonic acid water, and in solutions of ammonium salts. In the latter case a soluble magnesium ammonium salt is formed.

Exp. 136.—Burn magnesium. Boil water in a test-tube containing a piece of magnesium ribbon, and observe whether gas is evolved or not.

The magnesium of commerce acts slightly on boiling water. Next add a little hydrochloric acid. Magnesium chloride will be formed. What is the reaction?

Magnesium Chloride, $MgCl_2$ or $Mg{<}^{Cl}_{Cl}$.—This salt is obtained by neutralizing hydrochloric acid with magnesia alba, adding chlorine water to peroxidize any iron present, and then digesting for some time with slight excess of magnesia alba. The solution yields on evaporation, best over sulphuric acid, deliquescent crystals of the hydrous chloride, $MgCl_2 + 6H_2O$, which is very soluble in water and alcohol. If the hydrous salt is heated to expel the water partial decomposition takes place, and the residue consists of magnesium chloride mixed with some magnesium oxide. The oxygen of the water replaces chlorine, thus :

$$MgCl_2 + H_2O = MgO + 2HCl.$$
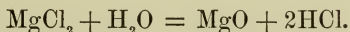
If, however, ammonium chloride is added to magnesium chloride, the solution may be evaporated without formation of magnesium oxide. The ammonium chloride is driven off by gentle ignition, leaving anhydrous magnesium chloride. In another method of preparing the anhydrous chloride the hydrous salt is dried by heating in a current of hydrochloric acid gas.

Magnesium chloride unites with other chlorides to form well-defined double salts, as for example, $KCl.MgCl_2 + 6H_2O$, $NaCl.MgCl_2 + H_2O$, and $2MgCl_2.CaCl_2 + 12H_2O$. Ammonium magnesium chloride, $NH_4Cl.MgCl_2 + 6H_2O$, separates in crystals when a solution of the two salts is evaporated. Ammonia does not precipitate solutions of this double salt, and when added to a solution of magnesium chloride only a portion of the magnesium separates as hydroxide, and the solution contains the double salt. If the magnesium hydroxide formed is dissolved by hydrochloric acid and ammonia again added, no

precipitate will form, owing to the presence of sufficient ammonium chloride to form the double salt.

Magnesium Oxide, Magnesia, MgO or Mg=O, is commonly made by heating magnesia alba, which loses water and carbon dioxide at a dull-red heat. The magnesia thus prepared is a very bulky white powder, which becomes more compact on intense ignition. Magnesia is used in medicine. It is a strong base, and neutralizes acids.

Magnesium Hydroxide, Mg(OH)$_2$ or Mg$<^{OH}_{OH}$.—Magnesia which has not been strongly ignited unites with water with evolution of some heat, but not nearly as much as in the slaking of lime. The hydroxide is also formed when potassium or sodium hydroxide is added to a solution of a magnesium salt. It occurs native as the mineral brucite.

Magnesium Sulphate, MgSO$_4$ or SO$_2<^O_O>$Mg, occurs native as epsomite, $MgSO_4 + 7H_2O$, and kieserite, $MgSO_4 + H_2O$. The former, known as Epsom salt, is named from the Epsom springs in England, from the water of which the salt was formerly manufactured. Magnesium sulphate has been made from serpentine, magnesite, and dolomite, but the Stassfurt salt mines, in which kieserite is abundant, yield the bulk of the salt in market. Magnesium sulphate is very soluble in water, 100 parts of water dissolving 27.73 parts of the anhydrous salt at 0°, and 73.8 parts at 100°. It crystallizes with seven molecules of water, six of which are given off below 150°; but the seventh molecule requires a temperature of 200° to expel it. If a solution of the salt is evaporated at 70° crystals are obtained with six molecules of water. Epsom salt has a bitter taste, is used as a purgative, and in dyeing with aniline colors, and in dressing cotton goods.

Zinc, Zn.

Atomic Weight, 65.4.   *Density,* 6.9 to 7.2.

The metal was unknown to the ancients, but they made brass by melting copper with zinc ores. Zinc was not smelted from its ores until the middle of the eighteenth century, although it was known as a distinct metal in the seventeenth century. The existence of the free metal in nature is doubtful. The chief ores of zinc are smithsonite, $ZnCO_3$; calamine, $Zn_2SiO_4 + H_2O$; and zinc blende, ZnS. In New Jersey the red oxide of zinc and franklinite (an oxide of iron, zinc, and manganese) are worked for zinc oxide. Zinc ores are first roasted to expel water, and in case of blends to change the zinc sulphide into oxide. The roasted ore, mixed with coal dust, is put into a hot fire-clay retort or muffle. The reduction of the zinc oxide by carbon only takes place at a temperature above the boiling point of zinc. The vapor of zinc is received in a suitable condenser connected with the retort.

Zinc is a white metal with a tinge of blue, and is capable of a high polish. It melts at 423° and boils at about 1000°. The density of cast zinc is 6.9, and of rolled or sheet zinc 7.2. Cast zinc breaks with a highly crystalline fracture: small pieces may, however, be hammered into bars. Between 100° and 150° it is malleable, and may be rolled into plates, which if not too thick may be rolled cold into sheets. At somewhat higher temperatures the metal becomes brittle again, and at 205° may be pulverized.

The zinc of commerce, commonly called spelter, usually contains small quantities of iron, lead, and arsenic, and traces of other metals. It dissolves readily in dilute acids. The solution is facilitated by impurities above mentioned, which form with the zinc galvanic couples.

Pure zinc is scarcely attacked by acids unless in contact with

another metal. The caustic alkalies and ammonia dissolve zinc with evolution of hydrogen, the reaction taking place more rapidly if a little copper or platinum is precipitated on the zinc.

Zinc does not tarnish in dry air; but in moist air a thin coating of basic carbonate forms, which prevents further corrosion.

Zinc is used for a variety of purposes where a cheap sheet metal is required that will resist atmospheric action. It is also used for the so-called galvanizing of iron. Large quantities of zinc are used in the manufacture of brass, which is an alloy of zinc and copper.

Zinc dust is a mixture of finely divided zinc and zinc oxide. It is formed in the smelting of zinc, and is used to remove oxygen from organic compounds.

Exp. 137.—Melt zinc in a crucible, and pour in a thin stream into water. If the metal is poured at temperatures little above its fusing point the granulated pieces will be thick. If, however, the metal is poured when very hot, thin irregular leaflets will be obtained.

Exp. 138.—Pour molten zinc into a clean dry mortar, and rub vigorously with the pestle. As soon as the metal becomes pasty it may be pulverized by rubbing.

Exp. 139.—Place a piece of common zinc in pure dilute sulphuric acid, and a similar piece of pure zinc in another portion of acid of the same strength. Note which dissolves the more rapidly. After half an hour add a drop of platinum chloride or copper sulphate to the acid with the pure zinc, and note result.

Exp. 140.—Warm some of the pulverized zinc of Exp. 138 with solution of potassium or sodium hydroxide, and add a drop of copper sulphate. Hydrogen will be given off slowly and zinc will dissolve. To prove the presence of zinc in the solution, add ammonium sulphide a white precipitate is evidence of zinc. Repeat the experiment, using instead concentrated ammonia water.

Zinc Chloride, $ZnCl_2$, or $Zn<^{Cl}_{Cl}$.—Finely divided zinc ignites spontaneously in chlorine, forming the chloride.

Anhydrous zinc chloride is a whitish deliquescent mass. It melts at a little above 100°, and distils at a high temperature. It has a strong attraction for water, and is used to separate the elements of water from organic compounds. The observed gas density of it corresponds to the formula $ZnCl_2$.

Zinc chloride is made by dissolving zinc or zinc oxide in hydrochloric acid. The solution becomes viscous on evaporation, and yields on cooling crystals of $ZnCl_2 + H_2O$. A high temperature is required to expel the last portion of the water. At the same time some zinc oxide is formed, thus:

$$ZnCl_2 + H_2O = ZnO + 2HCl.$$
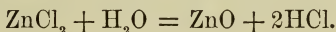
At a red heat anhydrous zinc chloride distils from the residue.

A concentrated solution of zinc chloride acts as a caustic on the skin, and destroys paper and cloth. Dilute solutions of the salt are used for disinfecting purposes. The Burnettizing process for preserving wood from decay consists in impregnating it with a solution of zinc in crude hydrochloric acid. Basic zinc chlorides or oxychlorides are formed when zinc oxide is boiled with solutions of the chloride. When the oxide is mixed with a concentrated solution of zinc chloride to a thick paste, the mass soon becomes warm, and hardens.

A mixture of zinc chloride and hydrochloric acid is much used in soldering with common solder, an alloy of tin and lead. The acid converts any film of metallic oxide present into chloride, which dissolves in the zinc chloride, thus cleansing the metal so that the molten solder will wet and adhere to it. Solder will not stick to rusty or oxidized metallic surfaces.

Exp. 141.—Dissolve zinc in hydrochloric acid, and evaporate the solution to the consistency of syrup. Pour a portion into a test-tube, and set aside to crystallize. Put some of the viscous chloride upon cloth and paper, and note the result.

Zinc Oxide, ZnO or Zn=0, is formed when the metal burns in air. It is manufactured directly from zinc ores by allowing the vapor of zinc obtained in the reduction to burn, and collecting the zinc oxide formed in suitable chambers. It is a white powder, largely employed as pigment known as zinc white. It does not blacken on exposure to hydrogen sulphide, like white lead. It is insoluble in water and soluble in acids.

Zinc Hydroxide, $Zn(OH)_2$ or $Zn{<}^{OH}_{OH}$, separates as a gelatinous precipitate on addition of sodium or potassium hydroxide to a solution of a zinc salt. It dissolves readily in excess of the caustic alkali.

Zinc Sulphide, ZnS, occurs as blende. When an alkali sulphide is added to a solution of a zinc salt a white precipitate is formed, consisting of hydrous zinc sulphide or zinc hydrosulphide, soluble in dilute hydrochloric and sulphuric acid, but insoluble in acetic acid. Hydrogen sulphide precipitates zinc sulphide from solutions containing but little free acid.

Zinc Sulphate, $ZnSO_4$ or $SO_2{<}^{O}_{O}{>}Zn$, is made on a large scale by roasting zinc blende, exhausting the mass with water, and evaporating the solution. The crystals (see Exp. 15) which separate have the composition $ZnSO_4 + 7H_2O$, and are known as white vitriol and as zinc vitriol. The crystals are isomorphous with Epsom salt. If the solution is concentrated at 50° the hydrate $ZnSO_4 + 6H_2O$ separates in crystals which are isomorphous with the corresponding magnesium salt. Zinc sulphate is very soluble in water. It is used in medicine, in dyeing, and for the preparation of other zinc compounds.

Cadmium, Cd.

Atomic Weight, 112.   *Molecule,* Cd.   *Density,* 8.6.

Cadmium was discovered independently by Stromeyer and Hermann in 1817. It is found in a few minerals, and in small quantities in many zinc ores. In the smelting of these ores the cadmium distils first, and mostly oxidizes in the receivers, forming a brown powder of impure oxide. This is mixed with charcoal and distilled, and the metallic product is again distilled. To free the cadmium thus obtained from the last portions of zinc, and also from copper and arsenic, it is dissolved in hydrochloric acid, and to the solution an excess of ammonium carbonate is added. The cadmium precipitates as basic carbonate, and the other metals remain in solution. The precipitate leaves on ignition the oxide, from which the pure metal is obtained.

Cadmium is a brilliant white metal, a little harder than tin, and very ductile and malleable. It melts at 315°, and boils at 860°. Its gas density at 1040° is 56.9 (Deville and Troost), which shows that its molecular weight at high temperatures is identical with its atomic weight. The metal is used in fusible alloys. An amalgam of cadmium and zinc is employed in filling teeth.

Cadmium Chloride, $CdCl_2$, is obtained by dissolving the metal or oxide in hydrochloric acid. The solution on evaporation yields crystals of $CdCl_2 + 2H_2O$, which effloresce in air.

Cadmium Iodide, CdI_2, is obtained by treating the metal with iodine and water. The anhydrous salt crystallizes from water in six-sided plates. It is one of the few metallic iodides soluble in alcohol. It is used in photography.

Cadmium Oxide, CdO, is obtained by the combustion of the

metal as a brown amorphous powder. It remai. s .sa blue-black powder consisting of microscopic octahedra when the nitrate is ignited.

Cadmium Hydroxide, $Cd(OH)_2$.—Potassium hydroxide produces in solutions of cadmium salts a white precipitate of the hydroxide, which is insoluble in an excess of the precipitant (difference from zinc hydroxide), but is readily soluble in ammonia.

Cadmium Sulphide, CdS, is found crystallized as the mineral greenockite. Hydrogen sulphide throws down from a solution of a cadmium salt a brilliant yellow precipitate of cadmium sulphide, insoluble in dilute acids. It is employed as a yellow pigment.

Cadmium Sulphate, $CdSO_4$, crystallizes with eight molecules of water when its aqueous solution evaporates spontaneously.

Mercury (Hydrargyrum), Hg.

Atomic Weight, 200.   *Molecule,* Hg.   *Density,* 13.59.

This element is also called quicksilver. It is found free in nature in small quantities. The chief ore of mercury is cinnabar, HgS. The metal is obtained by roasting the ore, whereby the sulphur is burned to dioxide, and the mercury is converted into vapor which is condensed in suitable chambers. In another process the ore is heated with lime, which combines with the sulphur, setting free the mercury which distils off.

Mercury is a silver-white lustrous liquid, having a density

of 13.594 at 0°. It forms when frozen a tin-white malleable solid, melting at $-39°.4$. Its boiling point is 357° at a pressure of 760 mm. Its vapor is colorless. At ordinary temperature the metal is slightly volatile, as may be shown by the silvering of gold-leaf which has been kept over mercury for some weeks. The density of mercury gas has been found to be 100, showing that the mercury molecule contains only one atom.

Pure mercury does not lose its lustre in air at ordinary temperature, but when heated to near its boiling point it slowly absorbs oxygen with formation of red mercuric oxide. Ozone, chlorine, and hydrogen sulphide quickly attack it. Hydrochloric acid is without action, and nitric acid dissolves it. Mercury may be converted into a fine dust when agitated with some substance which will coat the particles.

Mercury is used in thermometers and barometers, and is indispensable in experiments with gases. Large quantities are employed in the extraction of gold and silver from their ores. In the ordinary liquid form it is not poisonous, and has been swallowed without injury. When finely divided or in vapor it is poisonous. "Blue mass" or "blue pill" is made by triturating mercury with a fat or chalk until globules are no longer perceptible.

The mercury of commerce is liable to contain small quantities of other metals, which oxidize and form a film, which adheres to the surface of glass and interferes with its use for some purposes. The impurities are best removed by distilling the mercury with suitable precautions so that globules of the impure metal shall not be carried over with the vapor. For most uses in chemical and physical laboratories it can be sufficiently purified by treatment with nitric acid, which dissolves zinc, lead, and copper if present. The mercury and acid are violently shaken together, or the metal is poured in a thin stream into the acid: the object in either case is to expose a large surface of the metal to the acid.

The apparatus Fig. 77 is convenient when ᴍᴇʀᴄᴜʀy requires frequent cleansing. The tube B is made with several small holes in the end over C, so that mercury may fall in a spray into C. The tube C is 60 or 70 cm. long, and the tube D is of such length that mercury will fill C when in use to a depth of 3 or 4 cm. above the stopper which holds D. The tube E is similar to C, and about half as long. When the apparatus is first set up sufficient mercury is poured into A to fill the small tubes B, D, and F. C is then filled with dilute nitric acid and E with distilled water. The latter is to stop any acid which may possibly pass through D with the mercury. The mercury to be cleansed is poured into A, and is received dry in the jar G. If it is quite impure the operation must be repeated a number of times.

Mercury may be freed from dust by straining through a filter with a pin-hole in the apex.

Exp. 142.—Shake in a test-tube some mercury and a solution of ferric chloride to obtain the mercury in the form of dust. Wash with water by decantation. The fine particles may be united by boiling with strong hydrochloric acid.
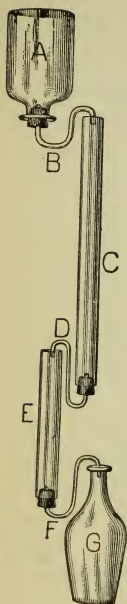
Amalgams are compounds or alloys of mercury with other metals. The amalgams with a large proportion of mercury are liquid, and often contain solid amalgams suspended in the mercury.

FIG. 77.

The latter can be separated by pressing it through wet leather, leaving the solid amalgam, which in some cases possesses a definite composition. Amalgams are commonly obtained by putting a clean metal in contact with mercury; sometimes the metal is placed in a solution of a mercury salt. Sodium and mercury unite with great violence, attended with a brilliant flash. Potassium combines without producing light. These amalgams are white and when containing more than one part of alkali metal to seventy of mercury are hard and brittle. By heating to 440°, the crystalline compounds HgK_2 and $HgNa_2$ are obtained. Copper, silver, gold, zinc, cadmium, and tin unite readily with mercury.

Exp. 143.—Warm mercury in a test-tube and drop in a small piece of clean sodium, and when combination ensues add more. If sufficient sodium is added the amalgam when cold will be solid and brittle. Place some of the amalgam in water. Hydrogen will be slowly evolved, the sodium decomposing the water.

Exp. 144.—*a.* Place a clean copper coin in a dilute solution of mercury nitrate. The mercury will precipitate on the copper, and some of the latter will dissolve.

b. Moisten a piece of sheet zinc with hydrochloric acid, then place it in contact with a globule of mercury.

c. Put a little mercury into a strong solution of silver nitrate containing a drop of nitric acid. A crystalline amalgam, known as the silver tree or arbor dianæ, will form rapidly.

Mercury forms two classes of compounds, viz., mercurous, in which mercury is univalent, as in Hg–Cl ; and mercuric, in which it is bivalent, as in $Hg < {Cl \atop Cl}$.

Mercurous Chloride, Calomel, HgCl or Hg–Cl, separates as a white powder when a soluble chloride is added to a solution of mercurous nitrate. It is obtained by subliming an intimate mixture of corrosive sublimate and mercury. Calomel is tasteless and insoluble in water and alcohol. It is much used in medicine. The density of its vapor has been found to be 117.6; theory requires for HgCl 117.7.

The molecular formula Hg_2Cl_2 or Cl–Hg–Hg–Cl has been assigned to mercurous chloride, mercury being viewed as a dyad in mercurous as well as in mercuric compounds. It has been supposed that mercurous chloride dissociates completely when gasified into mercuric chloride and mercury, which combine on cooling to form mercurous chloride again. The following facts support this hypothesis. When mercurous chloride is sublimed the product contains traces of mercuric chloride and minute globules of mercury. It has also been observed that calomel vapor amalgamates gold, thus showing the presence of free mercury in the vapor. The gas density

of a mixture of equal molecules of $HgCl_2$ and Hg is the same as the density of a gas composed of molecules of $HgCl$, thus:

2 volumes of mercuric chloride gas weigh   .   270.8
2 volumes of mercury gas weigh   200
_____
4 volumes of the mixed gases weigh   .   .   .   470.8
1 volume   "   "   "   " 117.7

It is obvious that the decomposition of mercurous chloride by heat does not decide the question whether its molecule is Hg_2Cl_2 or $HgCl$, for—

$$Hg_2Cl_2 = HgCl_2 + Hg, \text{ and}$$
$$2HgCl = HgCl_2 + Hg.$$
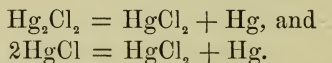
Recent experiments by Fileti show that mercurous chloride can exist as a gas, and that its molecule is $HgCl$. He found that when a mixture of mercurous and mercuric chlorides was heated to 400° no dissociation occurred, and that a gilded tube held in the gases was not amalgamated. His experiment proves that the presence of mercuric chloride prevents even a slight decomposition of mercurous chloride when gasified.

Mercurous Iodide, HgI or Hg–I, may be prepared by rubbing together 200 parts of mercury and 127 of iodine. It is a greenish powder, very slightly soluble in water, and which slowly decomposes into mercuric iodide and mercury.

Mercurous Fluoride, HgF or Hg–F, differs from the other mercurous halides in that it is soluble in water.

Mercurous Oxide, Hg₂O or HgO—HgO, is prepared by adding potassium hydroxide to a solution of a mercurous salt. It is a black powder that decomposes in light, and on warming into mercury and mercuric oxide.

Mercurous Sulphate, Hg₂SO₄ or $SO_2 {<} {O-Hg \atop O-Hg}$, falls as a powder when sulphuric acid is added to a solution of a mer-

curous salt. It is also formed when sulphuric acid is heated with an excess of mercury.

Mercuric Chloride, Corrosive Sublimate, $HgCl_2$ or $Hg{<}^{Cl}_{Cl}$, is formed by the direct union of mercury and chlorine, and also when mercury is dissolved in aqua regia. It is manufactured by heating a mixture of mercuric sulphate and common salt, which react thus:

$$SO_2{<}^O_O{>}Hg + 2Na{-}Cl = Hg{<}^{Cl}_{Cl} + SO_2{<}^{O-Na}_{O-Na}.$$
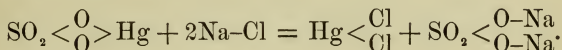
Mercuric chloride dissolves in 13.5 parts of water at 20°, and in 1.85 parts at 100°. It is more soluble in alcohol and ether than in water at ordinary temperature. It melts at about 265°, and boils at 293°, giving rise to a colorless gas having a density of 135.4, and corresponding to the molecular formula $HgCl_2$. It separates from solution in colorless crystals. When sublimed it forms a translucent crystalline mass. Corrosive sublimate is a violent poison. It is used in medicine, and for preserving skins, dried plants, and anatomical preparations. Reducing agents precipitate mercurous chloride from a solution of mercuric chloride, thus:

$$2Hg{<}^{Cl}_{Cl} + SO_2 + 2H{-}O{-}H = 2Hg{-}Cl + SO_2{<}^{OH}_{OH} + 2H{-}Cl.$$
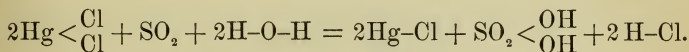
If stannous chloride is used, mercurous chloride separates, and is reduced to metallic mercury by an excess of stannous chloride:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4,$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$
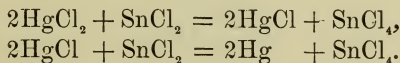
Mercuric Oxide, HgO or $Hg{=}0$. —As already stated, this compound is formed by direct union of its elements. It is more easily prepared by heating mercury nitrate, either alone

or mixed with mercury; red fumes are given off, and the oxide remains as a red crystalline powder. It turns black when heated cautiously, the red color reappearing on cooling, and at a red heat is completely decomposed. When potassium hydroxide is added to a solution of a mercuric salt mercuric oxide is obtained as an orange-yellow amorphous precipitate.

Mercuric Sulphide, HgS or Hg=S.—Mercury and sulphur combine when triturated or heated together to form mercuric sulphide. Soluble sulphides throw down from solutions of mercuric salts mercuric sulphide as a black precipitate. In case mercurous salts are present a mixture of mercuric sulphide and mercury results. The black amorphous sulphide changes to the red crystalline form when sublimed, and also when heated with a solution of an alkali polysulphide. Red mercuric sulphide is a valuable pigment known as vermillion.

Mercuric Sulphate, HgSO$_4$ or $SO_2<^O_O>Hg$, is prepared by heating mercury with an excess of sulphuric acid as long as sulphur dioxide is evolved. It is a white compound, which is decomposed by boiling water into the yellow salt Hg$_3$SO$_6$. This is called a basic salt, and as such may be formulated thus:

$$O<^{Hg}_{Hg}{>}^O_O>SO_2.$$
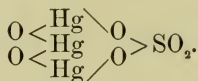
It may also be viewed as mercuric orthosulphate :

$$S<^{O_O>Hg}_{O_O>Hg}$$
$$^{O}_{O}>Hg.$$
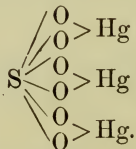
Exp. 145.—Dissolve mercury in an excess of cold dilute nitric acid of density 1.2 to obtain a solution of mercurous nitrate. Dilute the solu-

tion largely with water, and in case a yellow precipitate forms, add nitric acid until a clear solution results. Read the description of the mercury nitrates. To a portion of the solution add hydrochloric acid; the white precipitate is calomel, and will not dissolve in water. To another portion add sulphuric acid to obtain mercurous sulphate. Pour some of the mercurous nitrate into an excess of solution of potassium hydroxide to obtain mercurous oxide.

Exp. 146.—Dissolve mercury in an excess of hot strong nitric acid. To test for the presence of mercurous salt add some of the solution to nitric acid diluted with its bulk of water, and then add a few drops of hydrochloric acid. In case a precipitate of HgCl forms, add more nitric acid to the original solution, and heat again. Pour some of the mercuric nitrate into a solution of potassium hydroxide. The yellow precipitate obtained is mercuric oxide.

THE FIFTH GROUP.

The members of this group are nitrogen, phosphorus, arsenic, antimony, bismuth, vanadium, niobium, didymium, samarium, and tantalum.

Nitrogen, N.

Atomic Weight, 14. *Molecule, N_2.*

Nitrogen exists free in the atmosphere, of which it constitutes four fifths by volume. Its compounds occur in all plants and animals, and are essential components of all soils.

Nitrogen is a colorless, tasteless, and odorless gas, having a density of 14 (hydrogen as unity). It is but slightly soluble, 100 volumes of water absorbing 1.5 volumes of the gas at $1z°.6$.

Nitrogen liquefies at $-146°$ under a pressure of 35 atmospheres. Liquid nitrogen has a density of 0.885, and boils at $-194°.4$ under a pressure of one atmosphere. It solidifies at $-214°$ and 60 mm. pressure.

Under the influence of electric sparks the pressure of nitrogen gas diminishes slightly, according to Thomson and Trelfall, who attribute the change to the formation of an allotropic modification.

Free nitrogen is remarkable for its chemical inertness towards other elements under ordinary conditions. It does not combine directly with oxygen when a mixture of the two

gases is heated, and only slowly when subjected to electric sparks. As a constituent of the atmosphere, it serves to dilute the oxygen, and takes no part in the chemical changes of respiration and ordinary combustion. Nitrogen combines directly with boron, magnesium, vanadium, and titanium, to form nitrides.

Nitrogen is commonly prepared from air. Burning phosphorus will combine with most of the oxygen, and what remains may be removed by passing the gas through a tube filled with copper turnings heated to redness. Pure nitrogen is useful in experiments which must be conducted in an inert gas, that is, one which does not react with the substances to be tested. Many of the determinations of gas densities at high temperatures are made in an apparatus filled with nitrogen.

Exp. 147.—Ignite a dry bit of phosphorus in a shallow porcelain dish floating on water, and cover with a bell-jar. The phosphorus unites with oxygen to form phosphorus pentoxide, which combines with water to form phosphoric acid, a soluble compound. After the cloud has disappeared introduce a burning splinter or wax taper into the gas.

Ammonia, NH$_3$ or N$\Big\langle$$\begin{smallmatrix}\text{H}\\\text{—H}\\\text{H}\end{smallmatrix}$.—Nitrogen and hydrogen, under the influence of the silent electrical discharge, combine to form ammonia in very small quantity. It is formed in the decay of nitrogenous animal and vegetable matters, and also when these are subjected to dry distillation, that is, are strongly heated out of contact with air. The chief source of ammonia and its compounds is the ammoniacal liquor of gas-works. Bituminous coal contains about 2 per cent of nitrogen, most of which is converted into ammonia in the distillation of the coal in the manufacture of gas. Ammonia compounds exist in soils, and in minute quantities in the atmosphere.

Ammonia is a colorless, pungent gas, which condenses at low temperatures to a liquid boiling at $-33°.7$, and forms when frozen a transparent crystalline body, melting at $-75°$. It dissolves abundantly in water, forming a solution known as ammonia, ammonia water, aqua ammonia, and ammonium hydroxide. One gram (1 cc.) of water at $0°$ and 760 mm. pressure absorbs 0.875 gram or 1144 cc. of ammonia gas; at $10°$, 0.679 gram; at $20°$, 0.526 gram; and at $50°$, 0.229 gram. Ammonia water gives off the gas when open to the air, and all the gas is expelled by boiling the solution.

It may be assumed, for reasons which cannot be given now, that ammonia water is a solution of ammonium hydroxide, NH_4OH, formed by the union of NH_3 with H_2O. Both ammonia gas and ammonia water possess strong basic properties, neutralizing acids, and forming salts in which the univalent radical ammonium, NH_4, plays the same part as sodium or potassium, as illustrated by the following equations :

$$NH_3 + H\text{-}Cl = NH_4\text{-}Cl,$$
$$NH_4\text{-}OH + H\text{-}Cl = NH_4\text{-}Cl + H_2O,$$
$$K\text{-}OH + H\text{-}Cl = K\text{-}Cl + H_2O.$$

The first two equations show that the reaction between ammonia water and hydrochloric acid can be formulated on the hypothesis that ammonia water contains NH_4OH, and also on the assumption that ammonia water is simply a solution of NH_3.

The density of ammonia gas is 8.5; its molecular weight is, therefore, 17. Experiments have shown that 17 weights of ammonia contain 14 weights of nitrogen and 3 weights of hydrogen. Hence the molecule of ammonia is represented by NH_3. The gas is slowly but completely decomposed by passing electric sparks through it; and it has been found that 2 volumes of the gas yield when dissociated 1 volume of nitrogen and 3 volumes of hydrogen.

Ammonia does not burn in air unless some combustible gas is mixed with it. It may be burned in oxygen. The simpler tests for its presence are the odor, the bluing of red litmus paper, and the formation of a cloud with acid fumes.

Ammonia gas for experimental purposes is best obtained by heating concentrated ammonia water. In the arts it is set free from ammonium chloride or sulphate by means of slaked lime:

$$2NH_4\text{--}Cl + Ca{<}^{OH}_{OH} = 2NH_3 + Ca{<}^{Cl}_{Cl} + 2H_2O.$$

Exp. 148.—Heat concentrated ammonia water in a small flask, and pass the gas into an inverted cylinder, as indicated in Fig. 78. The hole in the rubber stopper in the cylinder should be about twice the diameter of the delivery-tube. When ammonia escapes abundantly into the air, lift the cylinder from the delivery-tube and place the stoppered end under water. The gas will be quickly absorbed, and water will fill the cylinder. The water will react alkaline with litmus.

Ammonia gas cannot be dried by calcium chloride as the two combine, but it may be freed from moisture by passing it through a tube filled with fragments of potassium hydroxide. The gas may be collected over mercury.

FIG. 78.

Exp. 149.—Neutralize 5 cc. of hydrochloric acid, diluted with its bulk of water, with ammonia, and evaporate the solution to dryness in a small porcelain dish. The product is ammonium chloride. Will the acid alone or the ammonia water leave a residue when evaporated?

Exp. 150.—Dilute 2 cc. of sulphuric acid with thrice its bulk of water, neutralize with ammonia, and evaporate the solution to dryness at a gentle heat. The product is ammonium sulphate. Represent the formation of it by an equation.

Exp. 151.—*a.* Triturate in a mortar a little of the ammonium chloride, obtained in Exp. 140, with calcium hydroxide. Observe odor, and test escaping gas with a moistened red litmus paper; also notice whether a cloud forms when a rod moistened with fuming hydrochloric acid is held over the mixture.

b. Repeat the experiment, using instead of ammonium chloride the ammonium sulphate of Exp. 150. Represent the reaction by an equation.

Exp. 152.—Add ammonium chloride to a solution of potassium hydroxide, and warm gently. In another test-tube heat a solution of ammonium sulphate to which potassium hydroxide has been added. In the first case potassium chloride is formed, in the second potassium sulphate. Formulate the reactions.

FIG. 79.

Exp. 153.—Heat strong ammonia water in a small flask, Fig. 79, and attempt to burn the ammonia gas escaping from tube *A.* Pass oxygen through *B* into the jacket tube *C*, and apply a flame to the jet of ammonia.

Diamide, Hydrazine, N_2H_4 or $\begin{matrix} N = H_2 \\ | \\ N = H_2 \end{matrix}$.—This compound of nitrogen and hydrogen was discovered in 1887. It is obtained by decomposing an organic compound containing nitrogen. Hydrazine is a colorless gas, with a peculiar odor, somewhat like that of ammonia. It is very soluble in water, and has a strong alkaline reaction. Hydrazine sulphate, N_2H_4. H_2SO_4, and the hydrochlorate, $N_2H_4(HCl)_2$, have been prepared.

Hydroxylamine, NOH_3 or NH_2–OH, is formed by the action of nascent hydrogen on some of the oxygen compounds of nitrogen. It is known only in solution or in combination with acids. It has strong basic properties, and, like ammonia and hydrazine, unites directly with acids. Hydroxylamine hydrochloride has the composition NH_2OHHCl. The aqueous solution of hydroxylamine decomposes on standing into nitrogen, ammonia, and water: $3NH_2OH = NH_3 + 3H_2O + N_2$.

Nitrogen Fluoride —When a solution of ammonium fluoride is electrolyzed, oily drops of a highly explosive compound are formed, which is supposed to be nitrogen fluoride.

Nitrogen Chloride, NCl_3.—This dangerous compound is prepared by inverting a thin flask filled with chlorine gas in a warm solution of ammonium chloride. The gas is absorbed, and impure nitrogen chloride in the form of oily drops separates. These may be collected in a lead dish and exploded by touching with a feather moistened with turpentine and held on along rod. It may also be obtained by electrolyzing ammonium chloride.

Pure nitrogen chloride is obtained as follows. The product obtained by acting on ammonium chloride with chlorine is washed with water to remove ammonium chloride, and then exposed for half an hour to chlorine. (Gattermann.)

Nitrogen chloride is one of the most violent explosives. It explodes in sunshine, and in contact with oil of turpentine, and when heated to 95°, and sometimes spontaneously.

Exp 154.—The apparatus, Fig. 80, consists of a tube A, 3 cm. in diameter and 18 cm. long, closed at the bottom with a rubber stopper, through which pass two glass tubes holding platinum wires, which are welded to strips of platinum foil in A. The stopper is fastened to a block of wood. The tube A is filled with a warm saturated solution of ammonium chloride, and a few drops of oil of turpentine are added The wires are connected with six Bunsen cells. Gas is evolved, and nitrogen chloride rises in minute particles, and explodes on coming in contact with the turpentine on the surface of the solution. A bell-jar over the apparatus prevents the turpentine from being thrown about. The experiment is easily and safely made.

FIG. 80.

Nitrogen Iodide, NI_3, is prepared by adding finely divided iodine (precipitated by pouring an alcoholic solution into water) to most con-

centrated ammonia water at 0°. The black powder is washed with ammonia water, alcohol, and ether. Dried in a current of cold air it explodes violently It is liable to explode under water The compound N_2I_5H results when weaker ammonia is used at common temperature. It leaves NHI_2 on long contact with water at ordinary temperature. The black explosive powder commonly prepared by treating powdered iodine with ammonia water is a mixture of the above compounds.

Exp 155.—Pulverize a few decigrams of iodine, and pour over it a tablespoonful of concentrated ammonia water. After a quarter of an hour collect the powder on a small filter and wash with cold water. Pin the filter with contents to a stick, and leave to dry where the explosion will do no harm. The dry black powder explodes when slightly jarred, and often spontaneously. The moist powder decomposes violently in boiling water.

Ammonium Chloride, NH_4–Cl, has long been known under the name of sal-ammoniac. It is formed by the combination of equal volumes of hydrogen chloride and ammonia—a striking illustration of the production of a solid from the union of invisible gases.

$$NH_3 + HCl = NH_4\text{–Cl}.$$

Exp. 156.—Place a jar of dry ammonia gas over a jar of dry hydrogen chloride. The gases will diffuse into each other, and a white powder will result.

Ammonium chloride is manufactured on a large scale by saturating hydrochloric acid with ammonia obtained by distilling the ammoniacal liquor of gas-works. The solution is evaporated and the salt is purified by recrystallization from hot water, or it is sublimed. It is also made by heating a mixture of common salt and ammonium sulphate, when sal-ammoniac sublimes and sodium sulphate remains:

$$2Na\text{-}Cl + SO_2{<}{O\text{–}NH_4 \atop O\text{–}NH_4} = 2NH_4\text{–}Cl + SO_2{<}{O\text{–}Na \atop O\text{–}Na}.$$

The sublimed sal-ammoniac of commerce is a tough, fibrous, translucent mass. The salt is obtained as a crystalline meal, when a solution is rapidly evaporated. Ammonium chloride crystallizes in cubes, octahedrons, and other forms of the regular system. At 0°, 28 parts and at 100°, 72.8 parts of the salt are soluble in 100 parts of water. A solution of the pure salt is neutral to test papers, but on boiling becomes slightly acid owing to partial dissociation and escape of ammonia. Ammonium chloride cannot exist in the gaseous state, and is resolved by heat into ammonia and hydrogen chloride gases, which recombine on cooling. When the mixed gases diffuse, the ammonia, being less dense than the hydrogen chloride, diffuses faster, and may be partially separated.

Exp. 157.—Heat sal-ammoniac in a test-tube, over the end of which is placed a moistened red litmus paper. The test paper will at first be colored blue by ammonia, and later acid fumes will redden it. Ammonium chloride will collect in the cooler part of the tube.

The density of the gas obtained by heating ammonium chloride has been found to be 13.35, a result which accords with the view that the salt does not exist in the gaseous state; thus:

2 volumes of	ammonia gas weigh		17.
2 " "	hydrogen chloride weigh		36.4
			———
4 " "	the mixed gases weigh		53.4
1 " "	" " "		13.35

Ammonium chloride is used in the preparation of ammonia, in dyeing, and for various other purposes in the arts. It is also used in medicine.

Ammonium Fluoride, NH_4F, is obtained by subliming a mixture of ammonium chloride and sodium fluoride. An aqueous solution may be prepared by neutralizing hydrofluoric acid with ammonia. On evaporation ammonia escapes, and hydrogen ammonium fluoride, $NH_4F.HF$,

crystallizes out. Neither of the salts can be preserved in glass, and their solutions etch glass.

Ammonium Bromide, NH_4Br, and Ammonium Iodide, NH_4I, are similar to the chloride. The iodide deliquesces in moist air, and slowly turns yellow owing to separation of iodine.

Ammonium Sulphate, $(NH_4)_2SO_4$ or $SO_2\!<\!{\begin{array}{l}O\text{–}NH_4\\O\text{–}NH_4\end{array}}$.—This salt is extensively manufactured by neutralizing sulphuric acid with ammonia obtained by heating the ammoniacal liquor of gas-works with lime. It forms transparent colorless crystals, isomorphous with those of potassium sulphate. It dissolves in less than twice its weight of cold water and in its own weight of boiling water. It melts at 140°, and at higher temperatures decomposes, giving off ammonia, water, nitrogen, and sulphur dioxide. Ammonium sulphate is employed in the preparation of ammonia compounds, and is valuable as a fertilizer.

Ammonium Monosulphide, $(NH_4)_2S$ or $NH_4\text{–}S\text{–}NH_4$, results when two volumes of ammonia gas and one volume of hydrogen sulphide are mixed, and cooled to −18°. It forms colorless crystals soluble in water, which decompose at ordinary temperature into ammonia and hydrogen ammonium sulphide. An aqueous solution of the monosulphide is prepared by dividing an ammonia solution into two equal parts, saturating one portion with hydrogen sulphide, and mixing the two solutions.

Hydrogen Ammonium Sulphide, HNH_4S or $H\text{–}S\text{–}NH_4$.— When a mixture of ammonia gas and hydrogen sulphide is cooled to 0°, this compound is formed in colorless crystals which are volatile at common temperature. A solution of hydrogen ammonium sulphide is made by saturating ammonia water with hydrogen sulphide. The solution gradually turns yellow owing to formation of higher sulphides, oxygen

is slowly absorbed from the air, and ammonium thiosulphate, sulphite, and sulphate are formed. On long standing the solution becomes colorless again and deposits sulphur, all the ammonium sulphide being decomposed.

The polysulphides $(NH_4)_2S_4$, $(NH_4)_2S_5$, and $(NH_4)_2S_7$ have been prepared.

A solution of ammonium sulphide is much used in chemical analysis to precipitate certain metals as sulphides, and also to dissolve the sulphides of some metals.

Constitution of Ammonium Salts.—The salts which ammonia forms with acids are regarded as containing the radical NH_4, since this can be transferred from one compound to another, and can be replaced by metals. Further, ammonium salts are isomorphous with potassium salts, NH_4 apparently having many properties in common with K. As examples of analogous compounds may be given NH_4–Cl, K–Cl; $SO_2 < {O-NH_4 \atop O-NH_4}$, $SO_2 < {O-K \atop O-K}$.

Exp. 158.—Drop some sodium amalgam into a concentrated solution of ammonium chloride. The mercury will swell up and become a pasty mass, which is supposed to be an alloy of mercury and ammonium formed by the ammonium, NH_4, replacing the sodium of the sodium amalgam. In the reaction sodium chloride is formed.

Ammonium amalgam decomposes rapidly, giving off hydrogen and ammonia.

Compounds of Ammonia with Metallic Salts.—Ammonia unites with a large number of salts to form compounds whose constitution is not well understood. Only a few of these will be noticed. The compound $2AgCl.3NH_3$ is formed when silver chloride is dissolved in ammonia, and also when the dry chloride is saturated with dry ammonia. On adding ammonia to a solution of copper sulphate a basic salt separates, which dissolves in excess of ammonia. The deep-blue solution if

concentrated deposits on standing crystals of the compound $CuSO_4.4NH_3 + H_2O$.

Mercurous-Ammonium Chloride, NH_3HgCl, is a black powder formed when precipitated mercurous chloride is exposed to dry ammonia. If a solution of ammonia is used, **dimercurous-ammonium chloride, NH_2Hg_2Cl,** is formed. **Mercuric-ammonium chloride, NH_2HgCl,** separates as a white precipitate when ammonia is added to a solution of mercuric chloride.

Oxides and Hydroxides of Nitrogen.

There are five oxides and three oxy-acids of nitrogen:

Nitrous oxide, N_2O	Hyponitrous acid, HNO ?
Nitric oxide, NO.	
Nitrogen trioxide, N_2O_3.	Nitrous acid, $NO-OH$.
Nitrogen tetroxide, N_2O_4.	
Nitrogen pentoxide, N_2O_5.	Nitric acid, NO_2-OH.

Nitric Acid, HNO_3 or NO_2-OH.—This acid is formed synthetically in small quantity when electric sparks pass through moist air. If dry air in a flask is subjected to a succession of sparks from an induction-coil red fumes of the compound NO_2 will be seen, and on adding water the color will disappear; the NO_2 and water reacting, as explained later, to form nitric acid. Traces of nitric acid are also found when hydrogen is burned in oxygen mixed with a little nitrogen. The source of nitric acid is nitrates. These salts are formed in the soil by the slow oxidation of nitrogenous organic matter in presence of alkali carbonates and calcium carbonate. Nitrification takes place best in not too wet a soil and in a warm climate.

Nitric acid is manufactured by heating a mixture of potas-

sium or sodium nitrate and sulphuric acid, and condensing the acid vapors in a cooled receiver:

$$NO_2-O-K + SO_2 <^{OH}_{OH} = NO_2-OH + SO_2 <^{O-K}_{OH}.$$

The acid thus prepared contains water derived from the water contained in the sulphuric acid, and in part from decomposition of a portion of the nitric acid by heat. To purify the product, it is mixed with its bulk of concentrated sulphuric acid and redistilled. The distillate is warmed, and a current of dry air passed through it to remove nitrogen tetroxide. In this way nitric acid, HNO_3, containing less than one per cent of water has been prepared. It is a colorless fuming liquid, which absorbs moisture from air, and is very corrosive. Its density at 15° is 1.53. When the pure concentrated acid is heated a portion decomposes into nitrogen tetroxide, which colors it red or yellow, and water and oxygen. It commences to boil at 86°, and the boiling point gradually rises to 120°.5. The residue contains 68 per cent of HNO_3, distils unchanged, and has a density at 15° of 1.414. A more dilute solution yields by distillation acid of the same strength. The ordinary pure concentrated nitric acid has a density of about 1.4. It may be preserved in the dark, but in strong daylight, especially in sunshine, it becomes red. A stronger acid known as *red fuming nitric acid* consists of HNO_3, a little water, and NO_2, and has a density of 1.50 to 1.53. It is more energetic in its action than the ordinary acid.

Concentrated nitric acid corrodes and oxidizes many organic substances, dissolves sulphur slowly with formation of sulphuric acid, and even oxidizes charcoal. When it acts upon certain organic compounds the radical NO_2 is substituted for hydrogen. Benzene, C_6H_6, for example, is converted into $C_6H_5NO_2$ or $C_6H_4(NO_2)_2$, according to the strength of acid used. Cotton (cellulose), $C_{12}H_{20}O_{10}$, when placed in a mix-

ture of fuming nitric acid and oil of vitriol, does not change in appearance, but is converted into gun-cotton or cellulose hexnitrate, $C_{12}H_{14}O_4(NO_3)_6$. The yellow stain which nitric acid produces on the skin and on cloth is due to the formation of a yellow nitrate or nitro compound.

Nitric acid is extensively used in the manufacture of metallic nitrates, aniline dyes, sulphuric acid, gun-cotton, and nitro-glycerine.

The hydroxides of pentavalent nitrogen are, theoretically, $N(OH)_5$, $NO(OH)_3$, and NO_2OH. Certain basic salts may be viewed as derivatives of pentabasic or tribasic nitric acid ; but the ordinary nitrates are derivatives of monobasic nitric acid. Nitric acid reacts with bases to form nitrates, thus :

$$NO_2{-}OH + K{-}OH = NO_2{-}O{-}K + H_2O.$$
$$2NO_2{-}OH + Ca {<}{OH \atop OH} = {NO_2{-}O \atop NO_2{-}O}{>}Ca + 2H_2O.$$

Metals dissolve in nitric acid with formation of nitrates, and at the same time nitrous fumes are evolved, a part of the acid being reduced to the lower oxides of nitrogen by the metal, or by the hydrogen which the metal replaces. If the acid is dilute and cold it will dissolve zinc, for example, without formation of red fumes, and the nascent hydrogen will convert part of the acid into ammonia, thus :

$$HNO_3 + 8H = NH_3 + 3H_2O.$$

The reduction is complete when a small portion of a nitrate is acted upon by hydrogen evolved from zinc in a solution of potassium or sodium hydroxide.

Exp. 159.—Place 40 grams of potassium nitrate in a pint retort, and add the amount of sulphuric acid required to form $HKSO_4$. Calculate the weight and number of cubic centimeters required of sulphuric acid, density 1.8, and containing 86 per cent of H_2SO_4. Support the retort on a lamp-stand, and heat cautiously with a lamp as long as acid distils.

The neck of the retort is thrust into a flask which rests in a water-pan, and is cooled by a wet towel, or by pouring water over it. Towards the close of the distillation red fumes will appear, and color the distillate.

Exp. 160.—Dilute the nitric acid of the previous experiment with its bulk of water, and neutralize with ammonia. Evaporate the solution, towards the last without boiling, until a drop taken out on a cold rod solidifies at once. Label the salt ammonium nitrate, and set aside for a future experiment.

Exp. 161.—*a.* Drop a few bits of pulverized zinc into concentrated nitric acid contained in a test-tube. Note observations.

b. Mix thoroughly 5 cc. of strong nitric acid with 60 cc. of water. Pour this dilute acid into a test-tube containing a few grams of pulverized zinc, and observe that the action is very different from that in *a.* After 15 to 30 minutes pour some of the solution into another test-tube, add potassium hydroxide in excess, heat, and test escaping vapors for ammonia.

Exp. 162.—Place pulverized zinc, not too little, and a solution of potassium hydroxide in a test-tube ; warm gently until hydrogen escapes freely. The gas will not react for ammonia if the potassium hydroxide used is free from nitrates and nitrites. Add one drop of nitric acid, and in a few minutes test for ammonia.

Exp. 163.—Place 50 cc. of red fuming nitric acid in a beaker, standing on a plate, which is partly filled with lime

Fig. 81.

water. Cover with a bell-jar, as shown in Fig. 81, and drop into the acid a piece of glowing charcoal. The charcoal will burn brilliantly on the surface of the acid.

Nitrates.

Potassium Nitrate, KNO$_3$ or NO$_2$–O–K.—This salt is also called saltpetre and potash nitre. The formation of nitrates in soils has already been noticed. Nitre is obtained from the nitrification of urine and manure in soil mixed with wood ashes to furnish the potassium. The process is carried out in artificial nitre beds, which formerly furnished much of the nitre used in Europe. The climate of portions of India is favorable to the formation of nitrates, and that country furnishes a very considerable portion of the potassium nitrate of commerce. At the present time potassium nitrate is manufactured from Chili saltpetre (sodium nitrate) and potassium chloride. These salts are dissolved in hot water, when they mutually decompose as follows :

$$\text{K–Cl} + \text{NO}_2\text{–O–Na} = \text{NO}_2\text{–O–K} + \text{Na–Cl.}$$

The sodium chloride separates from the hot solution and is removed, and the potassium nitrate crystallizes on cooling the solution. The separation depends upon the difference in solubility of the two salts. Potassium nitrate forms large rhombic crystals when a solution evaporates slowly, or a hot saturated solution cools slowly. A crystalline meal is obtained by rapidly boiling down a solution. The salt is very soluble in water, 100 parts of water dissolving at 0°, 13.3 parts of KNO$_3$; at 20°, 31.2 parts; at 100°, 247 parts; at 114°.1, 327.4 parts. The boiling point of the saturated solution is 114°.

Potassium nitrate is a powerful oxidizing agent, yielding its oxygen readily to combustible substances. It is used in fireworks, in the laboratory, in medicine, in salting meats, but chiefly in gunpowder. *Gunpowder* is an intimate mechanical mixture of nitre, sulphur, and charcoal. The explosive effect is due to the rapid liberation of gases in the burning of the

sulphur and charcoal, at the expense of the oxygen of the nitre.

Sodium Nitrate, Chili Saltpetre, $NaNO_3$ or NO_2-O-Na.— This nitrate is abundant in southern Peru, Bolivia, and northern Chili. It is largely used, as already stated, in the manufacture of potassium nitrate, and as a source of nitric acid. It is a valuable fertilizer. It closely resembles potassium nitrate in properties, but cannot be substituted for the latter in gunpowder, since it becomes moist in air.

One hundred parts of water at 0° dissolve 73 parts; at 40°, 102 parts; and at 100°, 180 parts of $NaNO_3$. The saturated solution boils at 120°, and contains 100 parts of water and 216 parts of the salt.

Ammonium Nitrate, NH_4NO_3 or NO_2-O-NH_4, is obtained by neutralizing nitric acid with ammonia or ammonium carbonate (see Exp. 160). The salt is decomposed by heat, as stated under nitrous oxide, p. 242. It is soluble in half its weight of water at common temperature, and is much more soluble in hot water.

Cupric or Copper Nitrate, $Cu(NO_3)_2$ or $\begin{matrix} NO_2-O \\ NO_2-O \end{matrix} > Cu$.—This salt is prepared by dissolving copper or copper oxide in nitric acid. The solution yields on evaporation deliquescent crystals of $Cu(NO_3)_2 + 3H_2O$, which are soluble in alcohol. The salt loses water and acid at a gentle heat, and is converted into a basic salt, and at a red heat cupric oxide remains.

Silver Nitrate, $AgNO_3$ or NO_2-O-Ag.—If a piece of silver is hung in cold nitric acid of density 1.2, the metal slowly dissolves without effervescence, the liquid becoming blue from the nitrous acid formed. If the acid is hot, the metal dissolves rapidly, and nitric oxide is evolved. The salt separates in large transparent crystals on evaporating and cooling the solution.

According to Kremers, 100 parts of water at 0° dissolve 121.9 ; at 54°, 500 ; and at 110°, 1111.0 parts of silver nitrate. It is also soluble in alcohol. Silver nitrate melts at 198°, and solidifies on cooling to a white fibrous mass. At a red heat it is completely decomposed. Its aqueous solution is neutral, and has a bitter metallic taste. It is used in photography and chemical laboratories, and in small doses as a medicine. It acts as a powerful caustic on the skin, turning it black, and destroying it. For use as a caustic it is cast into small sticks, and is called *lunar caustic.* Pure silver nitrate is not changed by light, unless in contact with organic matter, when it is decomposed, and a dark substance is formed. Indelible inks are made of silver nitrate and gum-arabic. The mark on the cloth turns black in sunshine or on warming. Better indelible inks are made of coal-tar blacks, which are not bleached by chlorine or potassium cyanide.

Auryl Nitrate, $AuO.NO_3$ or **$NO_2–O–Au=O$,** is prepared by digesting auryl hydroxide with nitric acid of density 1.40 on a water-bath. The solution is evaporated over caustic alkalies, which absorb the acid. By this method Schrottlaender obtained black crystals having the composition $5AuONO_3 + H_2O$.

Acid Auric Nitrate, $HNO_3.Au(NO_3)_3 + 3H_2O$, is obtained by treating auryl hydroxide with 3.6 parts of pure nitric acid of density 1.49, and heating gently for some hours on a waterbath. The yellow solution, after the particles of reduced gold have subsided, is decanted and cooled with ice and salt, or is evaporated somewhat at 60°–80°, and finally over lime and caustic soda. Large crystals separate, which may be kept unchanged in a tight-stoppered jar. The salt is decomposed by water into auryl hydroxide, $AuO.OH$.

Calcium Nitrate, $Ca(NO_3)_2$ or $\dfrac{NO_2–O}{NO_2–O} > Ca$. — This salt is prepared by neutralizing nitric acid with lime or calcium car-

bonate. It is the most abundant product of nitrification in soils, but because of its solubility and deliquescence in moist air it does not often appear in nature in the solid state.

Strontium Nitrate, $Sr(NO_3)_2$ or $\begin{matrix} NO_2-O \\ NO_2-O \end{matrix}>Sr.$ — This compound is used in pyrotechny for imparting a red color to flames. It crystallizes with four molecules of water, which it loses at $100°$.

Barium Nitrate, $Ba(NO_3)_2$ or $\begin{matrix} NO_2-O \\ NO_2-O \end{matrix}>Ba.$ — This salt is prepared by dissolving barium carbonate in nitric acid, and also by mixing concentrated hot solutions of barium chloride and sodium nitrate. Barium nitrate separates when the solution cools, and sodium chloride remains in solution. Barium nitrate forms anhydrous crystals, which are permanent in the air and are sparingly soluble in water. It is used as a reagent, and for making green lights.

Magnesium Nitrate, $Mg(NO_3)$, or $\begin{matrix} NO_2-O \\ NO_2-O \end{matrix}>Mg.$ — This salt is prepared by neutralizing nitric acid with magnesia alba. On evaporating the solution crystals separate, having the composition $Mg(NO_3)_2 + 6H_2O$, and which deliquesce completely in moist air. The salt is soluble in alcohol.

Zinc Nitrate, $Zn(NO_3)_2$ or $\begin{matrix} NO_2-O \\ NO_2-O \end{matrix}>Zn$ — This is a deliquescent salt, which crystallizes with six molecules of water, and which is soluble in alcohol.

Cadmium Nitrate, $Cd(NO_3)_2$ or $\begin{matrix} NO_2-O \\ NO_2-O \end{matrix}>Cd,$ crystallizes with four molecules of water. It is deliquescent, and soluble in alcohol.

Mercurous Nitrate, $HgNO_3$ or NO_2–O–Hg.—This salt is obtained by acting on mercury with cold nitric acid of density 1.2. After a time crystals having the composition $HgNO_3 + H_2O$ separate. The salt is soluble in a small quantity of warm water, but is decomposed by much water with formation of an insoluble basic salt. The presence of nitric acid prevents this decomposition, and to obtain a dilute solution of the salt the concentrated solution is added to dilute nitric acid. A solution of mercurous nitrate stains the skin at first purple and then black.

Mercuric Nitrate, $Hg(NO_3)_2$ or $\dfrac{NO_2-O}{NO_2-O} > Hg$.—A solution of this salt is obtained by dissolving mercury in nitric acid, and heating until calomel does not separate on adding a drop of the solution to dilute hydrochloric acid. The solution yields on long standing over oil of vitriol crystals of $2Hg(NO_3)_2 + H_2O$, and the syrupy mother-liquor has the composition corresponding to $Hg(NO_3)_2 + 2H_2O$. Both the crystals and solution are decomposed by water; at first a white basic salt separates, this becomes reddish, and if the washing with water is continued mercuric oxide remains. The white salt has the composition $3HgO.N_2O_5 + H_2O$.

Nitrous Acid, HNO_2 or NO–OH.—This acid has not been prepared in the pure state, but is supposed to be formed when nitrogen trioxide is passed into ice-water. A blue solution is obtained, which on warming gives off nitric oxide, nitric acid at the same time being formed :

$$3NO-OH = NO_2-OH + 2NO + H_2O.$$

The salts of nitrous acid are stable and important. They are distinguished from nitrates by giving off red fumes when treated with acids.

Potassium Nitrite, KNO_2 or **$NO-O-K$**, is a very soluble and deliquescent salt. It is best prepared pure by the mutual decomposition of silver nitrite and potassium chloride, thus:

$$NO-O-Ag + K-Cl = NO-O-K + Ag-Cl.$$

The silver chloride is removed by filtration, and the solution is evaporated in vacuum. Potassium nitrate when heated gives off oxygen, and is more or less completely changed to nitrite. The addition of lead to combine with the oxygen facilitates the conversion of the nitrate into nitrite.

Silver Nitrite, $AgNO_2$ or **$NO-O-Ag$**, is prepared by mixing hot concentrated solutions of potassium nitrite and silver nitrate. Silver nitrite separates as the solution cools. It is sparingly soluble in water.

Hyponitrous Acid.—By treating a solution of potassium nitrate with sodium amalgam, neutralizing the solution with acetic acid, and then adding silver nitrate, a precipitate of silver hyponitrite is obtained. Some chemists regard this salt as having the composition $Ag_2N_2O_2$, and the results obtained by others correspond to the formula $Ag_4N_4O_5$. The free acid is obtained in solution by decomposing the silver salt with dilute hydrochloric acid. It decomposes on boiling with evolution of nitrous oxide.

Nitrous Oxide, N_2O, is a colorless gas which condenses at $-88°$ under ordinary atmospheric pressure to a mobile liquid solidifying at about $-100°$. Liquid nitrous oxide is kept in iron flasks, and is a commercial article. The gas has a slight odor and sweet taste. At $0°$, 100 volumes of water absorb 130 volumes, and at $20°$, 67 volumes of the gas. Nitrous oxide has been found to contain 28 weights of nitrogen and 16 weights of oxygen, and to have a gas density of 22. These data show that the molecule is N_2O. When the oxygen is removed from two volumes of the gas two volumes of nitrogen are left. Nitrous oxide is the anhydride of hyponitrous

acid, and is probably produced when the latter decomposes, thus :

$$H_2N_2O_2 = N_2O + H_2O.$$

The oxide, however, does not unite with water to form an acid.

Nitrous oxide gas supports combustion, and most substances which burn in air burn with a brilliancy in the gas, recalling combustions in oxygen. A glowing splinter inflames in nitrous oxide, and phosphorus burns as in oxygen. Burning sulphur is extinguished in the gas unless heated almost to boiling. Equal volumes of hydrogen and nitrous oxide explode violently when ignited.

Nitrous oxide gas is used as an anæsthetic in dentistry and short surgical operations, where insensibility for a brief period only is required. When a mixture of air or oxygen and nitrous oxide is breathed for a short time a nervous excitement, often accompanied by laughter, is produced, and without loss of consciousness. Hence the name *laughing-gas* has been given to nitrous oxide. When the gas is to be inhaled it should be perfectly pure, and free from chlorine and nitric oxide.

Nitrous oxide is prepared by heating ammonium nitrate, part of the salt being decomposed thus :

$$O_2N\text{–}O\text{–}NH_4 = N\text{–}O\text{–}N + 2H_2O.$$

At the same time a portion dissociates into nitric acid and ammonia, which unite in the cooler part of the apparatus to form ammonium nitrate again :

$$NO_2\text{–}O\text{–}NH_4 = NO_2\text{–}OH + NH_3.$$

When ammonium nitrate is heated too rapidly it decomposes with explosive violence and formation of other products. Nitrous oxide is freed from nitric oxide by contact with a solution of ferrous sulphate, and from acid fumes by potassium hydroxide.

Exp. 164.—The flask A, Fig. 82, has a capacity of about 200 cc. Place
in it the ammonium nitrate of Exp. 160, and
in B a piece of red litmus paper. Heat A
cautiously, so as to avoid too rapid evolution
of gas, and collect the gas over water. Ob-
serve that the test paper in B at first turns
blue and later becomes red. Why? Do not
decompose quite all the salt in A, and when
through heating, remove the delivery-tube
from the water. The bottle B will contain
water and ammonium nitrate. The presence
of the latter may be made evident by evapo-
rating the solution cautiously.

Exp. 165.—*a.* Thrust a glowing splinter
into nitrous oxide.

b. Introduce into the gas on a chalk spoon
a bit of sulphur burning feebly.

c. By means of a lamp flame heat the sul-
phur so that it will burn in the air very

FIG. 82.

rapidly, and then thrust it into nitrous oxide. If the sulphur is hot
enough it will burn in the gas.

Exp. 166.—To show the volume of nitrogen remaining after the oxygen
has been removed from nitrous oxide (and from nitric oxide) the appara-
tus, Fig. 83, devised by Prof. E. H. Keiser* may be used. The experi-
ment is based upon the fact that glowing copper combines with the
oxygen of the oxides of nitrogen, and leaves the nitrogen free. The
following is Prof. Keiser's description of the apparatus:

A represents a gas burette for measuring the volume of the gas. B is
a gas pipette, which is filled with water. The connecting-tube C is made
of hard glass, and is 3 mm. internal diameter and from 10 to 12 cm.
long. It is completely filled with granular metallic copper, which has
been obtained in the reduction of the granular oxide in a current of
hydrogen. The copper is held in place by plugs of asbestos at each end
of the tube. To decompose the oxides of nitrogen this tube is heated to
a red heat with a Bunsen burner, and to prevent it from bending, a piece
of wire gauze is wrapped around the outside and secured by wires.

A measured quantity of nitrous or nitric oxide contained in the burette
A is passed over the heated copper by opening the pinch-cock and rais-

ing the reservoir tube of the burette. When the reservoir tube is lowered the gas is drawn back from the pipette. It now consists of nitrogen, and its volume may be readily determined. If nitric oxide has been

FIG. 83.

used the volume of the nitrogen will be exactly one half the original volume of the gas; while in case of nitrous oxide the volume of nitrogen will be the same as the volume of nitrous oxide taken.

Nitric Oxide, NO, is a colorless gas, which is distinguished from all other colorless gases by forming red fumes of nitrogen tetroxide when mixed with oxygen or air. As these fumes are irritating, the odor and taste of pure nitric oxide is unknown. It is less easily liquefied than nitrous oxide, and,

like all difficultly condensable gases, is but slightly soluble in water. Its gas density is 15, and it contains equal volumes of oxygen and nitrogen. Nitric oxide contains the same amount of oxygen as a like bulk of nitrous oxide, but does not support ordinary combustion, and the affinity between nitrogen and oxygen in NO appears to be greater than in N_2O. A hydrogen flame, burning sulphur, and a candle flame, are extinguished when placed in nitric oxide, and so is phosphorus when feebly burning, but when burning brilliantly in air it burns with increased brilliancy when plunged into nitric oxide. A mixture of nitric oxide and vapor of carbon disulphide burns with a dazzling light remarkable for its actinic rays.

Nitric oxide is commonly formed when metals are dissolved in nitric acid. It is prepared by acting on copper with nitric acid. Probably the change takes place in two stages, thus:

$$2NO_2\text{–}OH + Cu = \frac{NO_2\text{–}O}{NO_2\text{–}O} > Cu + 2H,$$
$$NO_2\text{–}OH + 3H = NO + 2H_2O.$$

Thus prepared, the gas is liable to contain nitrous oxide, from which it can be freed by passing the gas into a solution of ferrous sulphate which absorbs the nitric oxide. The solution when heated gives off pure nitric oxide.

Exp. 167.—Place some copper clippings in a generator (Fig. 52, p. 54), and pour in water until the end of the thistle-tube is covered; then add concentrated nitric acid, and from time to time more acid as required. Collect several bottles of the gas over water.

Exp. 168.—*a.* Lift a bottle of nitric oxide from the water-pan, and place in the red fumes a blue litmus paper. For explanation of acid reaction see NITROGEN TETROXIDE.

b. Introduce a burning splinter, and a bit of burning sulphur on a chalk spoon into the gas.

c. Ignite a bit of phosphorus held just above a jar of nitric oxide, and quickly plunge into the gas. It will be extinguished. Bring the

phosphorus into the air again, and allow it to burn more brilliantly than before; then put it into the gas.

Exp. 169 —Fill a tall cylinder with nitric oxide, cover the end of the cylinder with a ground-glass plate, and place upright on the table. Drop into the cylinder a thin glass bulb, containing a few cubic centimeters of carbon disulphide. Shake violently to mix the carbon disulphide vapor with the gas; remove the glass plate and bring a lamp flame near the mouth of the cylinder. If the gas has been collected over cold water it should be allowed to stand until it has the temperature of the room, as the carbon disulphide will not vaporize sufficiently at low temperatures.

Nitrogen Trioxide or Nitrous Anhydride, N_2O_3.—When starch is heated with nitric acid of density 1.3 to 1.35, red fumes are evolved which condense in a tube surrounded by a freezing mixture to a green liquid containing nitrogen trioxide and tetroxide. If nitric oxide is passed into the warmed liquid, and the vapors passed through a hot tube, and again cooled, pure nitrogen trioxide will be obtained. At $-10°$ it is an indigo-blue liquid, which gives off brownish-red vapors containing nitric oxide and nitrogen tetroxide.

Nitrogen Tetroxide, N_2O_4, or Nitrogen Dioxide, NO_2, is formed when one volume of oxygen is mixed with two volumes of nitric oxide:

$$NO + O = NO_2.$$

It is best prepared by heating lead nitrate, which decomposes as follows:

$$\begin{matrix} NO_2-O \\ NO_2-O \end{matrix} > Pb = Pb=O + 2NO_2 + O.$$

Pure nitrogen tetroxide is a liquid which solidifies to colorless crystals at $-9°$. At a few degrees above its melting point the liquid is colorless, but at $15°$ is orange-colored. It boils at $26°.7$, giving off brownish vapors, which become darker, and finally, at a higher temperature, almost black.

At low temperatures the density of the vapor has been found to approach that required by the formula N_2O_4. The density diminishes with rising temperature, and at 140° corresponds to NO_2. These results show that the molecules of N_2O_4 are dissociated by heat into molecules of NO_2. Nitrogen dioxide and water react at ordinary temperature to form nitric acid and nitric oxide, thus:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

This explains the acid reaction of the red fumes formed when nitric oxide mixes with air.

Exp. 170.—Place in a bell-jar over water one measure of nitric oxide, and quickly mix with it one measure of oxygen. The gases will combine, and at first expand owing to the heat evolved; then the red fumes will be rapidly absorbed by the water, and a small bulk of nitric oxide will remain, as may be proved by adding more oxygen. If the experiment is made with pure nitric oxide, and oxygen added slowly, nearly all the gas in the bell-jar will disappear.

Nitrogen Pentoxide or Nitric Anhydride, N_2O_5, is a white crystalline solid, which becomes yellow when gently warmed, and melts at about 30° to a dark-yellow liquid. It explodes when suddenly heated, and sometimes spontaneously at ordinary temperatures. It is prepared by acting on pure nitric acid with phosphorus pentoxide:

$$2NO_2\text{-}OH + \frac{PO_2}{PO_2}{>}O = \frac{NO_2}{NO_2}{>}O + 2PO_2\text{-}OH.$$

Nitrogen pentoxide combines with water to form nitric acid. It volatilizes in dry air. It combines with nitric acid to form *pernitric acid*, $N_2O_5 \cdot 2HNO_3$ or $\begin{matrix} NO_2\text{-}O\text{-}NO\text{-}OH \\ {>}O \\ NO_2\text{-}O\text{-}NO\text{-}OH \end{matrix}$.

Pernitric acid has a density of 1.64, and crystallizes at 5°.

Nitrosyl Chloride, NOCl, is formed by the combination of nitric oxide and chlorine. It is an orange-yellow gas at ordi-

nary temperature. It is the chloranhydride of nitrous acid, and reacts with a solution of potassium hydroxide, thus :

$$NO–Cl + 2K–OH = NO–O–K + K–Cl + H_2O.$$

Nitroxyl Chloride, NO_2Cl, results from the direct union of nitrogen tetroxide and chlorine, aided by heat. It is the chloranhydride of nitric acid.

Nitro-Hydrochloric Acid or Aqua Regia is a mixture of one measure of nitric acid with two to four measures of hydrochloric acid. The two acids decompose each other; chlorine is liberated, and $NOCl$ and possibly NO_2Cl are formed. Gold and platinum are insoluble in either nitric or hydrochloric acid alone, but dissolve in aqua regia. Its great solvent power is due to free chlorine, and to a less degree to $NOCl$ and NO_2Cl.

Exp. 171.—Place gold-leaf in fuming hydrochloric acid, and warm. Also try to dissolve gold-leaf in hot concentrated nitric acid. Mix the two acids containing the gold-leaf.

Constitution of the Oxygen Compounds of Nitrogen.—Oxygen acids, as already stated, are regarded as hydroxides, that is, compounds of hydroxyl, OH. Assuming that nitric acid is a hydroxide, we have the structural formula $NO_2–OH$. This view is supported by the reaction

$$NO_2–Cl + H–OH = NO_2–OH + H–Cl,$$

in which chlorine is replaced by hydroxyl.

The radical NO_2 will replace hydrogen not only in water, but also in other compounds, as for example :

$$\underset{\text{Benzene}}{C_6H_6} + NO_2–OH = \underset{\text{Nitrobenzene}}{C_6H_5–NO_2} + H_2O.$$

Regarding the constitution of the radical NO_2 little is

known besides its univalent character. $O=\overset{|}{N}=O$, $\overset{O}{\underset{O}{}}>N-$,

and $O=N-O-$ express different views. Nitrous acid is NO–OH, and NO is supposed to have the structural formula $O=N-$.

The oxides of nitrogen are regarded by some writers as having the constitution indicated by the following formulas :

$$N=N, \qquad -N=O, \qquad O=N-O-N=O,$$
$$\searrow\!\!\swarrow$$
$$O$$

Nitrous oxide   Nitric oxide   Nitrogen trioxide

$$-N\underset{\diagdown O}{\overset{\diagup O}{\Big\langle}}, \qquad O=N-O-N\underset{O}{\overset{O}{\diagup}}, \qquad \overset{O}{\underset{O}{\diagdown}}N-O-N\underset{O}{\overset{O}{\diagup}}.$$

Nitrogen dioxide   Nitrogen tetroxide   Nitrogen pentoxide

There are also other views of the structure of these compounds. Nitrogen trioxide and nitrogen pentoxide are the anhydrides of nitrous and nitric acids, and may be reasonably regarded as containing two acid radicals joined by oxygen.

Nitrogen tetroxide dissolves in cold water, with formation of nitrous and nitric acids, and hence is to be considered as the mixed anhydride of these acids, reacting with water, thus:

$$NO-O-NO_2 + HOH = NO-OH + NO_2-OH.$$

The Atmosphere is a mixture of about 21 volumes of oxygen and 79 volumes of nitrogen, with a varying proportion of aqueous vapor, and an average of 3 volumes of carbon dioxide in 10,000. It also contains traces of ammonia, nitrates, and nitrites, and at times ozone and hydrogen dioxide. The dust of ordinary air, visible when illuminated by a ray of light, is partly mineral matter, and partly of animal and vegetable origin. With the dust are germs which cause fermentation, putrefaction, and at times disease. Liquids, such as mutton-

broth and beef-tea, which soon become putrid in ordinary air, may be indefinitely preserved by boiling the fluid, and then plugging the mouth of the flask with cotton wool so as to keep out the dust and germs of the air. The vile odor noticed on entering a crowded and poorly-ventilated room is due to emanations of putrescible matter from the skin and lungs. This is, in part, the cause of the languor and head-ache often experienced in an overcrowded room. The increased amount of carbon dioxide in air which has been breathed repeatedly is not harmful, but it indicates the extent of the contamination.

The atmosphere is never free from vapor of water. This vapor is seldom saturated, that is, in such a condition that any slight increase of pressure or diminution of temperature will convert a portion of it into water ; but, on the other hand, the quantity present is rarely less than one tenth of the amount corresponding to saturation. Since the pressure of saturated vapor increases rapidly with rising temperature, the maximum quantity of water vapor possible in the atmosphere increases with the temperature, as is shown by the following table :

| Temperature. | | Weight of 1 liter of |
C.	F.	saturated water vapor.
$-18°$	$0°$	.0126 gram.
$0°$	$32°$	.0487 "
$10°$	$50°$	.0936 "
$20°$	$68°$	.1716 "
$30°$	$86°$	.3010 "
$40°$	$101°$	.5070 "

By dry air, we understand air which contains but a small portion of the water necessary to make a saturated vapor ; and by moist or damp air, that which contains a large proportion. When the water vapor present is in a condition of saturation, the *air* is commonly said to be saturated. It is obvious that a

dry air at a high temperature may contain much more water than a saturated air at a low temperature; e.g., a very dry air ($\frac{1}{10}$ saturation) at 40° C. contains four times as much vapor as a saturated air at −18° C. It is for this reason that the air in our dwellings is so very dry in winter unless a large quantity of water is evaporated in them. For this reason also a wetted cloth may lose water very rapidly in an atmosphere which would deposit water upon it at a few degrees lower temperature. Air for most experimental purposes may be dried sufficiently by calcium chloride or concentrated sulphuric acid, but to remove all traces of water long contact with phosphorus pentoxide is necessary.

The weight of one liter of pure dry air at 0° and 760 mm. is 1.2936 grams. The density of gases is very commonly referred to air as unity. In this book, as already stated, the density of gases is referred to hydrogen gas as unity. Dry air is 14.44 times heavier than hydrogen, hence the density, air = 1, multiplied by 14.44, equals the density compared with hydrogen.

The nitrogen and oxygen of the atmosphere are not in chemical combination, as is evident from the following facts. The two elements are not in atomic proportions, and they are not found to be in exactly the same proportion at all times and in all localities. When nitrogen and oxygen are mixed, there is no change in temperature or other evidence of chemical union. Pure water in contact with air absorbs oxygen and nitrogen in other proportions than found in the atmosphere, which would not be the case were the two gases in combination. In chemical deportment air is a mixture, its oxygen entering into combination the same as pure oxygen. Nitric oxide forms when mixed with air red fumes of the dioxide, but if mixed with nitrous oxide gas no red fumes appear, that is, nitric oxide combines with free oxygen, but does not withdraw oxygen from the compound N_2O. The oxygen of the air is the supporter of respiration and ordinary com-

bustion, the chief products in both cases being carbon dioxide and water.

Phosphorus, P.

Atomic Weight, 31. *Molecule*, P_4.

Phosphorus is a widely distributed element, occurring only in combination as in phosphates. It is an essential constituent of fruitful soils, and plants will not grow in soil free from it. From plants phosphorus passes to animals, whose juices and tissues contain small quantities of it, and whose bones are largely composed of calcium phosphate.

Phosphorus was first isolated by Brand in the year 1669, who obtained it from urine. Urine contains phosphates, and when evaporated a residue remains, from which phosphorus may be distilled out of contact with air. This was the only method of preparing phosphorus up to 1771, when Scheele obtained it from bones. Bones have since been the chief source of the phosphorus of commerce. In the manufacture of phosphorus bones are burned to remove the organic matter, and there remains bone-ash, which is about four fifths calcium phosphate, the rest being mostly calcium carbonate. The bone-ash is treated with sulphuric acid, when an insoluble calcium sulphate and a soluble acid calcium phosphate are formed, thus:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

The solution of the acid calcium phosphate is filtered, evaporated to dryness, and the residue is heated to change the acid salt into the metaphosphate:

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

The calcium metaphosphate is then intimately mixed with charcoal and heated to redness in earthen retorts, and the phosphorus vapor is condensed in water:

$$3Ca(PO_3)_2 + 10C = P_4 + Ca_3(PO_4)_2 + 10CO.$$

To obtain all of the phosphorus, sand is added to the mixture, and a calcium silicate remains in the retort. Phosphorus is also manufactured from mineral phosphates.

There are three allotropic forms of solid phosphorus, the common or octahedral, the red or amorphous, and the metallic or rhombohedral. The gas density of phosphorus at 1040° has been found to be 65; hence the molecule of phosphorus contains four atoms. At a white heat (1437°) Mensching and Meyer found the gas density to be 43.8. This result shows that the molecules of P_4 dissociate into molecules containing fewer atoms.

Common or Octahedral Phosphorus is almost colorless, and when slowly cooled from the liquid state is transparent, but if quickly cooled it is wax-like and translucent. At ordinary temperature it may be cut with a knife, but when cooled it is brittle. It has a density at 10° of 1.83. It melts at 44.3° and boils at 278°, forming a colorless vapor. The best solvent for common phosphorus is carbon disulphide. It is slightly soluble in some oils, but is insoluble in water and alcohol. Phosphorus ignites in air when heated to 60°, and may be inflamed by friction or a warm rod. Because of its inflammability it is kept under water. The familiar luminosity in the dark, or phosphorescence of phosphorus, from which it derives its name, is accompanied by a slow oxidation, and is best seen in a warm, damp atmosphere. A luminous mist rises from the phosphorus, and a peculiar odor is perceptible. It is remarkable that phosphorus is not luminous in pure oxygen below 20°, but on diluting with an indifferent gas or reducing

the pressure of the oxygen to $\frac{1}{5}$ of an atmosphere the phenomenon of phosphorescence is observed. According to Baker, phosphorus may be melted, and even distilled without taking fire in oxygen, which has been dried by long contact with phosphorus pentoxide to free the gas from all traces of moisture. From this it appears that water, even when present in minute quantity, plays some part in the combustion of phosphorus in oxygen or air.

Sticks of phosphorus which are kept under water and exposed to light become covered, first with an opaque white coating which gradually turns red and flakes off. This is red phosphorus. A solution of phosphorus in carbon disulphide on standing in sunlight deposits yellow particles of amorphous phosphorus, which later turn reddish.

Common phosphorus is a poison, large doses causing death in a few hours, and small doses a lingering and painful illness. The fumes are poisonous, and persons constantly exposed to them are liable to phosphorus-necrosis, a disease in which the bones of the jaw waste away. Red phosphorus is not poisonous. Phosphorus burns are painful, and often quite severe. They should be soaked for half an hour or longer in lime water to neutralize the acid formed in the combustion of the phosphorus, and then treated like an ordinary wound.

Red or Amorphous Phosphorus is formed when common phosphorus is heated to 240°–250°. Above 260° the red phosphorus changes to the colorless modification. The presence of a small quantity of iodine greatly facilitates the formation of red phosphorus. The change takes place rapidly when colorless phosphorus is heated in a closed vessel to about 300°, or above its boiling point. Thus obtained, red phosphorus is mixed with common phosphorus, which is removed by extraction with carbon disulphide.

The color of amorphous phosphorus is brownish red, but when finely divided and suspended in water it appears of a

bright scarlet color. Red phosphorus has a density of 2.1, is insoluble, and non-volatile. It is not phosphorescent, and does not oxidize in air. In its chemical deportment it is less energetic than ordinary phosphorus.

Rhombohedral Phosphorus is obtained by heating phosphorus with lead, in a sealed tube, to a red heat. After cooling, the lead is dissolved in nitric acid, and a mass of dark-red crystals remains. This modification of phosphorus has a density of 2.34, and requires a temperature of 358° to convert it into the ordinary form.

Phosphorus is used in chemical industries and in the laboratory, but its chief use is in the manufacture of matches. Friction matches were invented in 1832. Before this time fire was obtained by igniting tinder with sparks from a flint and steel, and also by igniting a mixture of potassium chlorate and sugar, to which sulphur was sometimes added, with strong sulphuric acid. The sulphur match of the present time is made by dipping the match-stick into sulphur, and then tipping the end with a mixture of phosphorus, glue, potassium nitrate or chlorate, and other substances. The mixture inflames when rubbed, and ignites the sulphur, which in turn sets fire to the wood. Paraffin is now substituted for sulphur to avoid the disagreeable sulphur fumes.

Exp. 172.—To purify common phosphorus place it in a dilute solution of potassium dichromate and sulphuric acid, and warm on a water-bath for some time. The impurities will be oxidized, and most of the coating which was on the phosphorus will disappear. Wash the solution from the beaker by means of a stream of water, and if the phosphorus is not colorless and clean, repeat the treatment. Melt it again under a fresh solution of dichromate and acid, and allow to cool slowly and quietly. Frequently it will remain liquid for a long time at a temperature much below its melting point. Phosphorus thus treated is nearly white, translucent, and exhibits on its upper surface a fern-like crystalline structure.

Exp. 173.—Melt some clean phosphorus under water in a beaker, and draw it (best by means of a rubber bulb) into a glass tube which is slightly conical. Pour cold water on the tube to solidify the phosphorus, and then transfer the tube to a beaker of cold water, and press out the stick of phosphorus. Preserve it in a bottle of water, and observe that after a day or two its surface becomes opaque.

Exp. 174.—Dissolve a clean piece of phosphorus in carbon disulphide and pour some of the solution upon filter paper. The solvent will soon evaporate, and the paper will glow in the dark and soon inflame. The solution of phosphorus will become turbid on standing in daylight.

Exp. 175.—Dry some phosphorus with filter paper, and heat it in a dry test-tube to boiling. But little red phosphorus will be formed. Add a fragment of iodine and heat again.

Exp. 176.—Examine commercial red phosphorus, and notice that it is moist, and that it reddens blue litmus paper. It contains a little common phosphorus, which oxidizes and absorbs moisture from the air, forming acids.

Heat a little red phosphorus in a narrow glass tube closed at one end, to convert it into the common modification. At first a gas may escape and take fire spontaneously. It is phosphoretted hydrogen, formed from the decomposition of phosphorous acid contained in the moist red phosphorus.

There are three compounds of phosphorus and hydrogen, PH_3, P_2H_4, and P_4H_2. The first is the analogue of ammonia, but is less basic. The second corresponds to hydrazine, N_2H_4.

Phosphine or Phosphoretted Hydrogen, PH_3, is a colorless gas with a peculiar disagreeable odor, and is but slightly soluble in water. It condenses to a liquid, boiling at about $-85°$, and solidifying at $-133°$. When pure it is not spontaneously inflammable. It is formed in a number of reactions, and is best obtained pure by decomposing phosphonium iodide with a solution of potassium hydroxide:

$$PH_4I + KOH = PH_3 + KI + H_2O.$$

The gas density of phosphine corresponds to the formula

PH_3. Phosphine is readily decomposed by electric sparks, and two volumes of the gas yield three volumes of hydrogen and half a volume of phosphorus vapor. Phosphine does not neutralize acid solutions to form salts, but unites with hydriodic acid gas, forming phosphonium iodide, PH_4I, in colorless crystals. This compound is decomposed by water into PH_3 and HI.

Liquid Hydrogen Phosphide, P_2H_4, is an unstable compound which takes fire in air. It is formed in small quantity, together with phosphine, as in the following experiment.

Exp. 177.—Place in a flask, Fig. 84, a solution of potassium hydroxide, density 1.30, a piece of phosphorus and a few drops of ether. The latter serves to displace the air in the flask. Heat cautiously until gas escapes freely from the delivery-tube, which dips under water. In order to obtain large bubbles of gas, a thin wide tube, made from a test-

FIG. 84.

tube, is fastened by means of a flexible rubber tube to the delivery tube. Many of the bubbles will inflame spontaneously, and form beautiful smoke-rings. The water in the pan should not be below ordinary tem-

perature, since cold water may condense the liquid hydrogen phosphide, to which is due the spontaneous ignition of the gas.

The gas formed in the experiment is a mixture of phosphine, hydrogen, and liquid hydrogen phosphide.

Phosphorus Halides.

Phosphorus Trifluoride, PF₃, is a gas obtained by the action of copper phosphide on lead fluoride. It condenses at low temperature and high pressure to a colorless liquid. It is decomposed slowly by water, with formation of phosphorous and hydrofluoric acids. A mixture of 2 volumes of the gas and 1 volume of oxygen explode violently when ignited by the electric spark, and form 2 volumes of the oxyfluoride, POF_3.

Phosphorus Pentafluoride, PF₅.—This compound is of great theoretical interest, as it shows the pentavalent character of phosphorus. It is formed by the action of arsenic trifluoride on phosphorus pentachloride :

$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5.$$

It is a colorless gas, possessing a density of 63. The molecular weight is, therefore, 126, corresponding to PF_5.

Phosphorus Trichloride, PCl₃, is prepared by acting on an excess of phosphorus with dry chlorine. It is a colorless, mobile liquid, boiling at 76°, and having a gas density of 68.5. With water it forms phosphorous and hydrochloric acids.

Phosphorus Pentachloride, PCl₅, results from the union of chlorine with the trichloride. It is a yellowish crystalline powder. It dissociates gradually when vaporized into equal molecules of PCl_3 and Cl_2. In the presence of the vapor of the trichloride the pentachloride is more stable, and its vapor has been found to have a density nearly that required by the formula, PCl_5. Phosphorus pentachloride changes in moist

air to the oxychloride, and with excess of water orthophosphoric acid is formed.

Phosphorus Oxychloride, Phosphoryl Chloride, POCl₃ or

$PO{\Large\langle}{\scriptstyle\substack{Cl\\ Cl\\ Cl}}$ —This compound is a colorless fuming liquid, boiling

at 107°, and with a gas density corresponding to its formula. It dissolves slowly in water, with formation of orthophosphoric and hydrochloric acids. It is formed in a number of reactions, of which may be mentioned the following:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$
$$3PCl_5 + P_2O_5 = 5POCl_3.$$

The **bromides** of **phosphorus** are analogous to the chlorides.

Phosphorus Di-iodide, PI₂ or **P₂I₄,** is prepared by dissolving phosphorus and iodine in proper proportions in carbon disulphide. On cooling the solution yellow crystals of the di-iodide separate, or the carbon disulphide may be evaporated, and the last traces of it expelled by a current of dry air. It is decomposed by water, with formation of phosphorous and hydriodic acids and a yellow substance.

Phosphorus Tri-iodide, PI₃, is a red compound obtained in the same way as the foregoing, only using more iodine. It reacts with water, thus:

$$PI_3 + 3H_2O = P(OH)_3 + 3HI.$$

The phosphorus halides are valuable reagents for making other compounds, and are especially useful in effecting the replacement of hydroxyl, OH, by a halogen atom. Examples of the reaction will be given under the constitution of phosphoric acids. There is a gradation of properties in these halides, with increasing atomic weights of the halogens. The pentafluoride is quite stable, the pentachloride dissociates on heat-

ing, and the pentabromide more easily, while the pentiodide of phosphorus does not exist.

Oxides and Hydroxides of Phosphorus.

Phosphorus suboxide, P_4O.	Hypophosphorous acid,	$H_2PO{-}OH$
Phosphorous anhydride, P_2O_3.	Phosphorous acid,	$P\begin{smallmatrix}{-}OH\\{-}OH\\{-}OH\end{smallmatrix}$
Phosphorus tetroxide, P_2O_4.	Hypophosphoric acid,	$O\begin{smallmatrix}PO<\begin{smallmatrix}OH\\OH\end{smallmatrix}\\P<\begin{smallmatrix}OH\\OH\end{smallmatrix}\end{smallmatrix}$
	Orthophosphoric acid,	$PO\begin{smallmatrix}{-}OH\\{-}OH\\{-}OH\end{smallmatrix}$
Phosphoric anhydride, P_2O_5.	Pyrophosphoric acid,	$O\begin{smallmatrix}PO<\begin{smallmatrix}OH\\OH\end{smallmatrix}\\PO<\begin{smallmatrix}OH\\OH\end{smallmatrix}\end{smallmatrix}$
	Metaphosphoric acid,	$PO_2{-}OH$

The oxides of phosphorus, with the exception of P_2O_5, are little understood, and are obtained in the pure state with difficulty. These lower oxides are formed when phosphorus is burned with an incomplete supply of air.

Phosphorus Pentoxide or Phosphoric Anhydride, P_2O_5, is prepared by burning phosphorus in dry air. It is a white amorphous powder which rapidly absorbs moisture from the air and deliquesces. It hisses when thrown upon water and dissolves with formation of metaphosphoric acid:

$$P_2O_5 + H_2O = 2HPO_3.$$

Phosphorus pentoxide is used for drying gases, and for removing the elements of water from acids in the preparation

of acid anhydrides, as, for example, N_2O_5. It is a valuable reagent in organic chemistry.

Exp. 178.—Ignite a piece of dry phosphorus in a capsule standing on a plate, and cover with a bell-jar. After the snow-like powder has settled, remove the bell-jar and capsule, and pour a little water on the phosphorus pentoxide which has collected on the plate. Test the solution with blue litmus paper. The white powder adhering to the sides of the bell-jar will soon liquefy.

Hypophosphorous Acid, H_3PO_2 or $H_2PO–OH$.—The barium salt of this acid is prepared by heating phosphorus with a solution of barium hydroxide as long as phosphine escapes:

$$3Ba(OH)_2 + 8P + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3.$$

The excess of barium hydroxide is converted by a stream of carbon dioxide into carbonate, which is removed by filtration. The solution yields on evaporation crystals of $Ba(PO_2H_2)_2 + H_2O$. The acid is obtained as follows. Sulphuric acid is added to a solution of the barium salt, and the mixture allowed to stand until the precipitated barium sulphate has subsided. The solution is siphoned off and evaporated, the temperature being raised at last to 130°. Crystals separate on cooling the liquid in a freezing mixture. The pure acid melts at 17°.4. Hypophosphorous acid and solutions of its salts absorb oxygen, and change to phosphoric acid and phosphates. The acid precipitates the metals gold, silver, and mercury from solutions of their salts. But one atom of hydrogen in hypophosphorous acid can be replaced by basic radicals, and therefore the acid must be considered monobasic.

Phosphorous Acid, H_3PO_3, $HPO(OH)_2$ or $P(OH)_3$.—This acid is prepared by adding gradually phosphorus trichloride to water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The vessel is placed in ice water to prevent the solution be-

coming too hot from the reaction. The solution is evaporated and finally heated to 180°. The thick liquid obtained solidifies after a time to a crystalline mass. Phosphorous acid melts at 70° and deliquesces in air. When heated it decomposes thus:

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

Its aqueous solution absorbs oxygen from the air, and resembles hypophosphorous acid in reducing action. It is dibasic under ordinary circumstances, forming salts, such as Na_2HPO_3. There are, however, organic derivatives of a tribasic phosphorous acid, as for example tri-ethyl phosphite, $P(OC_2H_5)_3$.

Hypophosphoric Acid, $H_4P_2O_6$, is formed together with phosphorous and phosphoric acids by the slow oxidation of phosphorus in moist air. The sodium salts are $Na_4P_2O_6 + 10H_2O$, $Na_3HP_2O_6 + 9H_2O$, and $Na_2H_2P_2O_6 + 6H_2O$.

Phosphoric Acids.—Phosphorus pentahydroxide, $P(OH)_5$, the hypothetical hydroxide of pentavalent phosphorus, is unknown; but compounds, which may be viewed as derived from it by removal of the elements of one or more molecules of water, are well-known acids, viz.:

Orthophosphoric acid

Metaphosphoric acid

$$O=P\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right.$$
$$O=P\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right.$$

$$- \quad HOH \quad =$$

$$O=P\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$$
$$O$$
$$O=P\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$$

Diphosphoric acid

Orthophosphoric acid is tribasic, and forms salts in which all three hydrogen atoms are replaced, and it is therefore assumed to contain three hydroxyl groups. This accords with the simplest view of the reaction between the chloranhydride, $POCl_3$ and water, thus:

$$PO\left\langle\begin{array}{c|c|c}Cl & H & OH \\ Cl+H & OH \\ Cl & H & OH\end{array}\right. \quad = \quad PO\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right. \quad + \quad 3HCl.$$

The formula $PO(OH)_3$ represents all that is known of the constitution of orthophosphoric acid, and does not require us to assign a valence to phosphorus, and thus a structure to the radical PO.

Metaphosphoric acid may be viewed thus, $\begin{matrix}O\\O\end{matrix}\!\!>\!P-OH$,

or the valence of phosphorus may be left undecided, and the structural formula PO_2-OH given. It will be observed that this is analogous to nitric acid. Diphosphoric acid, because of its derivation from the ortho-acid, may be assumed to contain the radical PO, and, without expressing the valence of phosphorus, it may be formulated thus:

$$O\left\langle\begin{matrix}PO<\begin{matrix}OH\\OH\end{matrix}\\PO<\begin{matrix}OH\\OH\end{matrix}\end{matrix}\right.$$

It is remarkable that either two or four, and never three,

atoms of hydrogen are replaced in the formation of diphos-
phates. There are salts which correspond to more complex
phosphoric acids.

The orthophosphates are distinguished by the following re-
actions. Silver nitrate produces in solutions of the normal
and acid salts a yellow precipitate of silver orthophosphate,
Ag_3PO_4. Ammonium molybdate throws down from a solution
of orthophosphate in nitric acid a heavy yellow precipitate of
ammonium phospho-molybdate.

Metaphosphoric acid coagulates a solution of albumen, the
other phosphoric acids do not.

Diphosphoric acid is distinguished from orthophosphoric by
producing a white granular precipitate in a solution of silver
nitrate, and from metaphosphoric acid by the fact that it does
not precipitate albumen.

Orthophosphoric Acid, H_3PO_4 or $PO{\Large\langle}{\small\begin{matrix} OH \\ OH \\ OH \end{matrix}}$, is obtained by

dissolving common phosphorus in warm nitric acid of
density 1.20. A more concentrated nitric acid should not
be used on account of danger of explosion. The solution is
evaporated and heated as long as acid fumes escape. Phos-
phoric acid is manufactured from bone-ash, the calcium
being separated as sulphate by means of sulphuric acid. The
process yields a product containing a small quantity of mag-
nesia, and often other impurities. When an aqueous solution
of phosphoric acid is evaporated, and the residue heated to
150°, but not hotter, a viscous mass remains, which has the
composition H_3PO_4, and which crystallizes on standing, or
quickly if a crystal of the acid is added. The crystals melt at
38°.6, and deliquesce in moist air. A solution of phosphoric
acid has an agreeable acid taste.

Trisodium Orthophosphate, Na_3PO_4 or $PO\begin{cases}O-Na \\ O-Na. \\ O-Na\end{cases}$—This salt

is prepared by adding the required amount of sodium
hydroxide to a solution of disodium phosphate. On evapora-
tion crystals of $Na_3PO_4 + 12H_2O$ separate. These lose water
on heating, and are converted into the anhydrous salt, which
is not decomposed at a red heat. A solution of trisodium
phosphate reacts alkaline, and absorbs carbon dioxide from the
air. The reaction in presence of sufficient carbon dioxide is
as follows:

$$Na_3PO_4 + CO_2 + H_2O = HNa_2PO_4 + HNaCO_3.$$

Disodium Orthophosphate, Na_2HPO_4 or $PO\begin{cases}O-Na \\ O-Na, \\ OH\end{cases}$ is the com-

mon phosphate of soda. It is prepared by adding sodium
carbonate to a solution of orthophosphoric acid as long as car-
bon dioxide escapes. The solution yields on evaporation crys-
tals having the composition, $Na_2HPO_4 + 12H_2O$. The salt is
very soluble in water, and, although an acid salt, reacts alka-
line to litmus. It is much used in the preparation of other
phosphates.

Monosodium Orthophosphate, NaH_2PO_4 or $PO\begin{cases}O-Na \\ OH \\ OH\end{cases}$.—This

compound results when solutions of common sodium phos-
phate and orthophosphoric acid are mixed. Crystals contain-
ing one molecule of water of crystallization separate when the
solution is evaporated. The salt has an acid reaction.

Silver Orthophosphate, Ag_3PO_4, separates as a yellow pre-
cipitate on adding silver nitrate to solutions of either of the
sodium orthophosphates:

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$
$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$
$$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3.$$

The nitric acid set free in the last two reactions renders the solutions acid. Silver phosphate is soluble in nitric acid and in ammonia.

Ammonium Sodium Orthophosphate, NH_4NaHPO_4 or $PO \begin{cases} O-NH_4 \\ O-Na \\ OH \end{cases}$.—This compound is commonly known as micro-cosmic salt. It is obtained by mixing solutions of sodium and ammonium phosphates, and also by the following process. Common sodium phosphate, 6 or 7 parts, and 2 parts of sal-ammoniac, are dissolved in boiling water. The salt separates in crystals with four molecules of water as the solution cools. The mother-liquor contains common salt.

$$Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl.$$

By recrystallization with addition of ammonia the salt is freed from sodium chloride. It loses its water at a gentle heat, and at a red heat fuses and is converted into sodium metaphosphate. Microcosmic salt is used as a flux in blow piping.

Tricalcium Orthophosphate, $Ca_3(PO_4)_2$ or $\begin{matrix} PO \begin{cases} O \\ O \end{cases} > Ca \\ \begin{cases} O \\ O \end{cases} > Ca \\ PO \begin{cases} O \\ O \end{cases} > Ca \end{matrix}$.—This calcium phosphate separates as a gelatinous hydrous precipitate on addition of sodium phosphate to an ammoniacal solution of calcium chloride. It is the chief mineral constituent of bones. It occurs abundantly in nature in combination with calcium chloride and fluoride in the mineral apatite.

It is insoluble in water, and is decomposed by sulphuric acid with formation of monocalcium phosphate and calcium sulphate.

Dicalcium Orthophosphate, $Ca_2H_2(PO_4)_2$ or Hydrogen Calcium Orthophosphate, $HCaPO_4$.—This compound is precipitated when calcium chloride is added to a solution of sodium phosphate.

Tetrahydrogen Calcium Orthophosphate, $H_4Ca(PO_4)_2$ or

$$PO\begin{smallmatrix}\diagup OH \\ \diagdown OH\end{smallmatrix}$$
$$\begin{smallmatrix}O\\ O\end{smallmatrix}\diagdown_O^O>Ca.$$
$$PO\begin{smallmatrix}\diagup OH \\ \diagdown OH\end{smallmatrix}$$

—This salt is obtained by dissolving either of the foregoing calcium phosphates in the requisite amount of phosphoric acid. It crystallizes, on spontaneous evaporation, in scales containing one molecule of water. It is also formed when tricalcium phosphate is treated with acids. The fertilizer known as " superphosphate of lime" is made by treating bones with sulphuric acid. It is a mixture of tetrahydrogen calcium phosphate, calcium sulphate, and organic matter. Tetrahydrogen calcium phosphate dissolves without decomposition in much water, but when 10 to 40 parts of water are added, it decomposes with separation of hydrogen calcium phosphate. Also, on heating the concentrated aqueous solution the hydrogen calcium phosphate separates, and redissolves again on cooling.

Ammonium Magnesium Orthophosphate, NH_4MgPO_4 + $6H_2O$ or $PO\begin{smallmatrix}\diagup O-NH_4 \\ \diagdown O\end{smallmatrix}>Mg$ + $6H_2O$.—This double salt separates as a

white precipitate when an ammoniacal solution of magnesium chloride and ammonium chloride is added to a solution of an orthophosphate. The precipitate is insoluble in water con-

taining ammonia, but is readily soluble in acids. It is obtained in the separation of magnesium, and also of phosphorus, in chemical analysis. It is converted by ignition into magnesium pyrophosphate, $Mg_2P_2O_7$.

Diphosphoric, Pyrophosphoric Acid, $H_4P_2O_7$ or $O\begin{cases} PO <\begin{smallmatrix} OH \\ OH \end{smallmatrix} \\ PO <\begin{smallmatrix} OH \\ OH \end{smallmatrix} \end{cases}$.

—This acid is formed when orthophosphoric acid is heated for some time to 215°. The sodium salt is easier to prepare pure, and is made by heating common sodium phosphate :

$$PO \begin{cases} O{-}Na \\ O{-}Na \\ OH \end{cases} \quad PO < \begin{smallmatrix} O{-}Na \\ O{-}Na \end{smallmatrix}$$
$$\qquad\qquad\quad - H_2O = O \qquad\qquad$$
$$PO \begin{cases} OH \\ O{-}Na \\ O{-}Na \end{cases} \quad PO < \begin{smallmatrix} O{-}Na \\ O{-}Na \end{smallmatrix}$$

Sodium pyrophosphate is soluble in water, and does not change to orthophosphate on boiling unless a stronger acid is added. When silver nitrate is added to a solution of sodium pyrophosphate, a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, separates.

Metaphosphoric, Glacial Phosphoric Acid, HPO_3 or $PO_2{-}OH$, remains as a glassy mass when pyrophosphoric acid is heated to redness. The molten mass solidifies on cooling to a colorless glass. Metaphosphoric acid dissolves slowly in water, and deliquesces in moist air. In solution it changes slowly, or rapidly if heated, to orthophosphoric acid.

Arsenic, As.

Atomic Weight, 75.   *Molecule,* As_4.

Arsenic occurs in the free state in abundance in some localities, but is more commonly found in combination, as in

the minerals mispickel, FeSAs, realgar, As_2S_2, and orpiment, As_2S_3. Arsenic is found in most iron pyrites, and is often contained in sulphuric acid manufactured from pyrites, and in substances prepared by means of such acid.

The metallic arsenic of commerce is either the native arsenic from the mines, or the product obtained by heating mispickel, which is decomposed thus:

$$FeSAs = FeS + As.$$

It usually has a dark-gray coating, due to oxidation. It may be purified by sublimation out of contact with air. Metallic arsenic is sold under the name of *cobalt*, a term derived from the German word *Kobold*, the demon of the mines. Cobalt, the element resembling nickel, is usually found in combination with arsenic.

Arsenic has a grayish-white metallic lustre, a density of 5.7, and is crystalline and very brittle. It volatilizes when heated without previous fusion, but may be fused at a dull-red heat, under increased pressure, in a sealed tube. The vapor of arsenic has a yellow color and a disagreeable garlic odor, supposed by some writers to be due to a lower oxide of arsenic. The gas density of arsenic at a red heat has been found to be 150, corresponding to the molecule As_4. The density diminishes with increasing temperature, and at a white heat (1437°) Mensching and Meyer have found it to be 94.5.

There are two, and perhaps three, amorphous modifications of arsenic. When arsenic is sublimed in a current of hydrogen, or in a tube sealed at one end, it condenses near the heated part in the crystalline form, and beyond as a black vitreous coating, while further on a yellow deposit* is formed,

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* The writer has observed that commercial arsenic gives a yellow sublimate on heating, but that a sample, which has been heated until it

according to Bellendorff, which quickly turns gray. These two forms of amorphous arsenic have a density of 4.7, and change at about 360° into the crystalline form.

Arsenic oxidizes slowly in moist air, losing its metallic lustre, and becoming dark-gray. According to Geuther, the product of the oxidation is arsenious oxide. Heated in air or oxygen, arsenic burns with a peculiar white flame, arsenious oxide being formed. It dissolves readily in nitric acid.

Exp. 179.—Heat a little arsenic in a tube closed at one end until it is bright, and after it is cool transfer to another tube. Sublime it slowly, and observe the three modifications. If the black and gray amorphous forms are gently heated they will become crystalline.

Arseniuretted Hydrogen, Arsine, AsH_3, is a colorless, highly poisonous gas, with an odor somewhat different from that of arsenical vapor. It is obtained by dissolving zinc arsenide, Zn_2As_3, in dilute sulphuric acid, or in greater purity when sodium arsenide, Na_3As, is dissolved in water or very dilute hydrochloric acid.

Arsene is formed in acid solutions containing arsenic, from which hydrogen is evolved, and passes off with the hydrogen. Arsenious oxide and arsenic acid are reduced by nascent hydrogen, as follows:

$$As_4O_6 + 24H = 4AsH_3 + 6H_2O.$$
$$H_3AsO_4 + 8H = AsH_3 + 4H_2O.$$

Arsine burns with a bluish-white flame, with formation of water and arsenious oxide. It is decomposed by heat into its constituents. Chemically, it closely resembles phosphine, but differs from the latter in that it does not combine with acids to form salts.

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remains bright on cooling, does not give a yellow-colored deposit. Whether there is a yellow modification of arsenic, or whether the sublimate in question is due to impurities, requires investigation.

Exp. 180.—Place 20–30 grams of arsenic-free granulated zinc in the generator of the Marsh apparatus, Fig. 85, and pour in dilute sulphuric acid, and a drop or two of platinum solution to facilitate the action between the acid and zinc. The escaping gas is dried by means of the calcium chloride tube. The portion of the hard glass tube over the lamps is wrapped with wire gauze to keep it in shape when hot. After the air is completely expelled from the apparatus ignite the jet of hydrogen, and heat the tube by the lamp flames. If no dark deposit appear

FIG. 85.

in the tube beyond the heated portion after some time, the reagents are free from arsenic. Next add a solution containing a few milligrams of arsenious oxide to the acid in the funnel tube, and allow this acid solution to drop slowly into the generator. After a time an arsenical mirror will be seen in the tube. This is amorphous arsenic. If the current of hydrogen is not too rapid, and but a few milligrams of arsenic are added to the acid in the generator, all of the metal will be deposited in the tube in from two to four hours. To find the weight of the arsenic cut off the length of tube containing the mirror and weigh. The metal can then be removed by heat, or by solution in nitric acid, and the tube cleaned, dried, and again weighed. The difference in the two weights gives the amount of metallic arsenic. This method of detecting arsenic is remarkable for its extreme delicacy, $\frac{1}{1000}$ of one milligram of arsenious oxide producing in this form of the Marsh apparatus a distinct mirror.

After obtaining a deposit in the tube from a few milligrams of ar-

senic, add a solution of 20–30 milligrams of arsenious oxide to the generator, and sufficient acid to make the hydrogen flame half an inch or longer. The flame will have a whitish tinge, and if a cold piece of porcelain is held in the flame a dark coating of arsenic will be deposited. The AsH_3 is decomposed by the heat of the flame, and part of the metal condenses on the cold surface.

Arsenic Trifluoride, AsF_3, is prepared by distilling in a leaden vessel a mixture of equal parts of calcium fluoride and arsenious oxide with four parts of pure sulphuric acid free from water. It is a colorless, fuming liquid, boiling at 63°. In contact with the skin it produces deep, painful sores.

Arsenic Trichloride, $AsCl_3$, is formed by the direct union of its elements. It is a very poisonous, fuming liquid, with a boiling point of 134°. Its observed gas density corresponds to the formula $AsCl_3$. It mixes with a little water, and is decomposed by much water, with formation of hydrochloric acid and arsenious oxide, which separates in minute crystals. A solution of arsenious oxide in concentrated hydrochloric acid probably contains arsenic trichloride.

Arsenic Di-iodide, AsI_2, is a dark-red substance which is soluble in alcohol and ether. It oxidizes readily on exposure to air, and is decomposed by water, with separation of arsenic in the form of a black powder. **Arsenic Tri-iodide, AsI_3,** is prepared by subliming a mixture of 1 part of metallic arsenic and 3 parts of iodine. It forms brilliant red crystals, soluble in water and alcohol. It is used in medicine. **Arsenic Pentiodide, AsI_5,** is obtained, according to Sloan, by heating arsenic and iodine in the proportions required by the formula to 150° for an hour and a half in a vessel filled with carbon dioxide.

Oxides and Hydroxides of Arsenic.

Arsenious anhydride, As_4O_6.

Orthoarsenic acid,
$$AsO\begin{cases} OH \\ OH \\ OH \end{cases}$$

Arsenic anhydride, A_2O_5.

Diarsenic acid,
$$O\begin{cases} AsO < {OH \atop OH} \\ AsO < {OH \atop OH} \end{cases}$$

Metarsenic acid, $AsO_2–OH$.

The aqueous solution of arsenious oxide doubtless contains arsenious acid, which has not, however, been isolated. There are salts of orthoarsenious acid, $As(OH)_3$, and of metarsenious acid, $AsO.OH$.

Arsenious Oxide or Anhydride, As_4O_6, is the arsenic or white arsenic of commerce. It is also called arsenic trioxide and arsenious acid. It is obtained in large quantities, as a waste product, in the roasting of arsenical ores, the vapors of it being condensed in large chambers. The crude product is purified by sublimation. If the vapors are conducted into a receiver, where the temperature is but little below that required to volatilize the oxide, vitreous arsenic, the amorphous form, is obtained ; but when the condensation occurs in a cool chamber, a white crystalline powder results. Both forms of arsenious oxide are commercial articles.

The amorphous form of arsenious oxide is a transparent, colorless solid, like glass in appearance. It gradually becomes opaque white, owing to the change to the crystalline condition. There are two crystalline forms of arsenious oxide, the rhombic, which is occasionally obtained by sublimation, and the octahedral, which commonly results when the vapor is cooled. Arsenious oxide volatilizes at about $218°$, forming a colorless vapor. Its gas density has been determined at temperatures from $571°$ to $1560°$, and found to be nearly 198, the calculated gas density of the compound As_4O_6. Arsenious oxide is but slightly soluble in water, the vitreous variety being more soluble than the crystalline. It dissolves abundantly in hot concentrated hydrochloric acid, and the solution on cooling deposits octahedral crystals. It forms with fuming sulphuric acid the compound $As_2(SO_4)_3 + SO_3$. Arsenious oxide is used in the manufacture of arsenical compounds. Its poisonous qualities are well known. Two to four grains are a fatal dose, and even one grain is dangerous.

Exp. 181.—Heat very cautiously a small piece of metallic arsenic in an open inclined tube, 6–10 mm. in diameter. Arsenious oxide will

condense in the cool part of the tube in small brilliant octahedral crystals, best viewed with a magnifying glass.

Exp. 182.—Place arsenious oxide in a narrow hard-glass tube, closed at one end, and above the oxide a piece of charcoal. Heat the latter to glowing, and, by inclining the tube in the flame, slowly sublime the oxide, and at the same time keep the charcoal red hot.

Exp. 183.—*a.* Heat rapidly arsenious oxide in a narrow tube closed at one end. Note fully all observations. *b.* Place a little arsenious oxide on a watch-glass, cover with another glass, and warm with a small flame, taking care to sublime the oxide very slowly. The crystals which form on the upper watch-glass are best seen under a microscope.

Potassium Arsenite.—When an excess of arsenious oxide is treated with a solution of potassium hydroxide, an acid potassium arsenite is formed, and, if alcohol is added to the solution, after some days crystals of $2KH(AsO_2)_2 + H_2O$ separate. If this salt is boiled with a solution of potassium carbonate, carbon dioxide is evolved, and potassium arsenite, $KAsO_2$, is formed, which may be precipitated from the thick liquid by alcohol. A solution of potassium arsenite, known as Fowler's solution, is used in medicine.

Copper Arsenite, Scheele's Green, CuHAsO₃, is prepared by adding an ammoniacal solution of arsenious oxide to a solution of copper sulphate. It has a yellowish-green color. **Paris Green** is chiefly composed of a compound of copper arsenite and acetate, having the composition $3Cu(AsO_2)_2 + Cu(C_2H_3O_2)_2$. It is extensively used as a green pigment, and also as a poison. It is made by boiling a mixture of verdigris (a basic copper acetate), arsenious oxide, and water.

Arsenic Anhydride or Arsenic Pentoxide, As₂O₅, is prepared by heating arsenic acid to dull redness. It dissolves slowly in water, with formation of orthoarsenic acid. At high temperatures it decomposes into arsenious oxide and oxygen.

When metallic arsenic burns in air only arsenious oxide is formed, and not the pentoxide, differing in this respect from phosphorus, which burns to the pentoxide.

Arsenic Acid is prepared by digesting arsenious oxide with nitric acid or aqua regia. The solution is evaporated to dryness, and the residue gently heated. If it is dissolved in water, and the solution evaporated to a thick liquid and cooled, crystals having the composition $2AsO(OH)_3 + H_2O$ separate. These crystals are converted at $100°$ into anhydrous orthoarsenic acid, $AsO(OH)_3$. This at $180°$ changes to diarsenic acid, $H_4As_2O_7$, and at $200°$ metarsenic acid, $HAsO_3$, is formed. These last two acids dissolve in water, with formation of the ortho-acid. The arsenates closely resemble the corresponding phosphates. Arsenic acid and its salts are employed in dyeing, and in the manufacture of dyes.

Arsenic Disulphide, As_2S_2, occurs native as realgar, having a red or orange color. An impure disulphide is manufactured by heating together arsenious oxide and sulphur. It is used in white Indian fire, which is a mixture of one part of disulphide and twelve parts of nitre.

Arsenic Trisulphide, As_2S_3, occurs as a golden-yellow mineral. It forms a bright-yellow precipitate when hydrogen sulphide is passed into an acid solution of arsenious oxide. It dissolves in a solution of ammonium sulphide, with formation of ammonium sulpharsenite, $(NH_4)_3AsS_3$.

Arsenic Pentasulphide, As_2S_5. —When hydrogen sulphide is passed into a solution of arsenic acid no precipitate appears at first, but the arsenic acid is reduced to As_2O_3, which is then converted into trisulphide:

$$2H_3AsO_4 + 2H_2S = As_2O_3 + 5H_2O + 2S,$$
$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

If arsenic trisulphide is digested with a yellow solution of sodium sulphide, and the solution evaporated, crystals of sodium sulpharsenate,

$Na_3AsS_4 + 7\frac{1}{2}H_2O$, separate. Dilute acid added to a solution of this salt causes a precipitation of arsenic pentasulphide:

$$2Na_3AsS_4 + 6HCl = As_2S_5 + 6NaCl + 3H_2S.$$

Antimony (Stibium), Sb.

Atomic Weight, 120. *Density,* 6.7.

Antimony is found in the free state in small quantities. It occurs in a number of minerals, the most important being stibnite, Sb_2S_3, which is the chief source of the antimony of commerce. The metal is obtained either by melting the ore with wrought-iron, which combines with the sulphur; or the ore is roasted, whereby the sulphur burns to dioxide, and the antimony is converted into oxide, which is reduced by fusion with coal. The molten metal after a process of purification is poured, together with an easily fusible slag, into a thick iron mould. The antimony solidifies before the slag, and assumes on its upper surface a peculiar fern-like structure, required in commerce as evidence of its purity.

Antimony is a brilliant white metal, hard, and so brittle that it is easily pulverized. It crystallizes in rhombohedrons, melts at 425°, and vaporizes at a red heat, but too slowly for a determination of its gas density. The metal preserves its lustre in air unless heated, when it burns with formation of a fume of oxide. It dissolves in hot concentrated hydrochloric acid, but better in aqua regia. Antimony combines directly with sulphur and the halogens. It is extensively used in the arts in alloys, to impart hardness, and in making tartar emetic, and a few other medicinal preparations.

Alloys of Antimony.—*Type metal* is an alloy of lead, tin, and antimony, to which copper is sometimes added. *Britannia metal* or *pewter*, a cheap alloy used as a basis for silver-plated

ware, consists of tin with about 10 per cent of antimony.
Anti-friction metal, used for lining journal-boxes, is made of
antimony, tin, and a little copper.   Sometimes lead is added
to the alloy.

Antimony Hydride or Stibine, SbH_3, is formed under the
same conditions as its analogue arsine, and is found in hydro-
gen evolved from acid solutions containing antimony.   Stibine
is best prepared by treating a pulverized alloy of 2 parts of
antimony and 3 of zinc with dilute sulphuric acid.   It crys-
tallizes at $-102°$, as a snow-white mass, melting at $-91°$ to a
colorless liquid, which decomposes partially at low tempera-
tures ($-56°$ to $-65°$), with separation of antimony.   It boils at
$-18°$.   The gas is odorless, slightly soluble in water, burns
with a greenish-white flame and a fume of antimony oxide.
If a piece of cold porcelain is held in a hydrogen flame con-
taining stibine, a black mirror of antimony is deposited.   The
gas is completely decomposed at a red heat, and metallic anti-
mony may be obtained as a mirror in a tube after the method
employed with arsine.

Antimony Trichloride, $SbCl_3$.—A concentrated solution of
this compound has long been known as butter of antimony.
It is used as a caustic, and for imparting a brownish tint to
metallic surfaces.   Antimony trichloride is formed when
chlorine is passed over an excess of the metal, and also when
antimony or antimony sulphide is dissolved in hydrochloric
acid.   On distilling the solution water and acid first pass over,
and then the antimony trichloride.

Antimony trichloride forms a transparent crystalline mass,
melting at 72°, and boiling at 223°.   Its vapor is colorless,
and has been found to have a density of 117, theory requiring
113 for $SbCl_3$.   On pouring an acid solution of the trichloride
into water a white precipitate forms, known as *powder of al-*

garoth, which is a mixture of oxychloride and oxide of antimony. The precipitation is prevented by tartaric acid, or by a large excess of hydrochloric acid. If the trichloride is mixed with a small quantity of water, and the excess of the trichloride removed by washing with ether, **Antimonyl Chloride, SbOCl,** remains. This, on heating, leaves the oxychloride, $Sb_4O_5Cl_2$.

Antimony Pentachloride, SbCl$_5$, is formed by the direct union of its elements, with evolution of light and heat. It is prepared by saturating the fused trichloride with chlorine. It is a colorless or yellowish fuming liquid, which partially decomposes on distillation into trichloride and chlorine. With a little water it forms the hydrate $SbCl_5 + 4H_2O$; with more water the oxychloride SbO_2Cl, which is converted in antimonic acid by hot water. When mixed with a large excess of water a clear solution results.

The compounds SbF_3, SbF_5, $SbBr_3$, and SbI_3 are known. The pentabromide and pentiodide do not appear to exist.

Oxides and Hydroxides of Antimony.

Antimonious anhydride, Sb_4O_6.

Antimony tetroxide, Sb_2O_4.

Antimonic anhydride, Sb_2O_5.

Orthoantimonious acid, $Sb\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$

Orthoantimonic acid, $SbO\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$

Diantimonic acid, $O\left\{\begin{matrix}SbO<^{OH}_{OH}\\SbO<^{OH}_{OH}\end{matrix}\right.$

Metantimonic acid, $SbO_2\text{·}OH$.

Antimonious Oxide, Sb$_4$O$_6$, is formed, together with tetroxide, when antimony burns in air, and is obtained pure by washing algaroth powder with hot water, and finally with a

solution of sodium carbonate, whereby all the chlorine is removed. The gas density of antimonious oxide, at a temperature of about 1560°, has been found in two experiments to be 283.6 and 289; theory requires 288 for Sb_4O_6. It is both basic and acidic in character. It dissolves in sulphuric acid, with formation of $Sb_2(SO_4)_3$, and in a boiling solution of sodium hydroxide, to form sodium antimonite, SbO.ONa. Antimonious oxide dissolves readily in a solution of hydrogen potassium tartrate (cream of tartar), with formation of antimony potassium tartrate (tartar emetic), $C_4H_4SbKO_7$. This compound yields, with dilute nitric acid, orthoantimonious acid, $Sb(OH)_3$. Antimonious oxide is soluble in a solution of tartaric acid.

Antimony Tetroxide, Sb_2O_4.—This oxide is formed when antimonic acid is strongly heated, and is prepared by oxidizing antimony with concentrated nitric acid and igniting the residue. It is infusible and non-volatile, and is dissolved by hydrochloric acid with great difficulty.

Antimonic Anhydride or Antimony Pentoxide, S_2O_5, is obtained by treating antimony with an excess of strong nitric acid, evaporating off the acid, and then heating the residue to a temperature below redness. It is a pale-yellow powder, practically insoluble in water and nitric acid, but slowly soluble in hydrochloric acid. It reddens moist litmus paper.

Antimonic Acid.—When a solution of a metantimonate is treated with sulphuric or nitric acid a white powder separates, which, according to some authorities, has the composition $SbO(OH)_3$, and according to others $Sb(OH)_5$. It loses water at 175°, and is converted into metantimonic acid, $SbO_2.OH$. The potassium salt of this acid is prepared by fusing a mixture of 1 part of antimony and 4 parts of potassium nitrate. The mass is treated with tepid water to remove potassium nitrite, and the white powder obtained is boiled for an hour or two with water to dissolve it. The solution on evaporation leaves a gummy mass, having the composition $2KSbO_3 + 5H_2O$, and soluble in warm water.

Potassium Diantimonate, $K_4Sb_2O_7$, is prepared by fusing potassium antimonate with three times its weight of potassium hydroxide, dissolving the product in water, and evaporating the solution. Deliquescent warty crystals separate, which are decomposed by water into free alkali and hydrogen potassium diantimonate, $H_2K_2.Sb_2O_7 + 6H_2O$. This last salt is easily soluble in water at 40° to 50°, and in solution decomposes into gelatinous antimonate.

Hydrogen Sodium Diantimonate, $H_2Na_2Sb_2O_7 + 6H_2O$.—This sodium salt is remarkable for its insolubility, sodium salts as a rule being soluble. It separates as a crystalline precipitate when hydrogen potassium diantimonate is added to a solution of a sodium salt.

It will be observed that the metantimonates stand in the same relation to the diantimonates as the metaphosphates to the diphosphates, and hence are thus named. The metantimonates are, however, often termed antimonates, and the diantimonates metantimonates.

Antimony Trisulphide, Sb_2S_3, occurs native in lead-gray crystals of stibnite. Hydrogen sulphide produces in an acid solution of an antimonous salt an orange-red amorphous precipitate of antimony trisulphide containing water. The precipitate loses water on heating, and is converted at 200° into the black crystalline form. Antimony trisulphide fuses easily, and may be volatilized in an atmosphere of nitrogen, It dissolves in hydrochloric acid, with evolution of hydrogen sulphide. It is soluble in solutions of potassium or sodium hydroxide and alkali sulphides. Antimony sulphide is employed in the preparation of other antimony compounds, and is used for vulcanizing rubber.

Antimony Pentasulphide, Sb_2S_5, is prepared by passing hydrogen sulphide through a solution of the pentachloride containing tartaric acid, and also by decomposing a solution of a sulphantimonate with an acid. It is a yellowish-red powder, soluble in alkalies and alkali sulphides. It is decomposed by heat into trisulphide and sulphur. It is a sulphur-

acid anhydride, uniting with metallic sulphides to form sulphosalts, most of which have the general formula R_3SbS_4, analogous to the ortho-phosphates.

Sodium Sulphantimonate, $Na_3SbS_4 + 9H_2O$, is formed when either of the sulphides of antimony is dissolved in a solution of sodium sulphide, and also when a mixture of antimonious oxide and sulphur is boiled with a solution of sodium hydroxide. The solution is evaporated until crystals form on cooling, and is then allowed to cool slowly. The crystals are colorless or pale yellow, and are soluble in 2.9 parts of water at 15°.

Bismuth, Bi.

Atomic Weight, 208. *Density,* 9.8.

The chief source of this comparatively rare metal is native bismuth. Bismuth has a reddish-white color, a brilliant lustre, and is highly crystalline. It melts at 270°, and volatilizes at very high temperatures. It dissolves readily in nitric acid and aqua regia.

Its salts are used in medicine, and the metal itself enters into the composition of various fusible alloys. *Wood's fusible metal,* melting at 60°.5, is composed of 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium. Fusible alloys, melting at certain temperatures, are used for safety plugs in steam-boilers, and when, from increase of pressure, the temperature of the steam reaches the melting point of the alloy, the plug opens and allows steam to escape.

Fusible metal is valuable for making casts, on account of its low melting point, and its property of expanding in solidifying, thus making a good cast.

Bismuth in chemical properties is more basic and more metallic in character than antimony. Its halides resemble the halides of antimony and phosphorus in that they are decomposed by water into oxy-compounds. No bismuth compound of hydrogen is known.

Bismuth Dichloride, BiCl$_2$, is obtained by heating the tri-chloride with metallic bismuth, and by other processes. Its molecular weight is not known, as it decomposes on heating into the trichloride and bismuth.

Bismuth Trichloride, BiCl$_3$, is formed when the metal is burned in chlorine. It is a white fusible substance. Its gas density has been found to accord with the formula BiCl$_3$. Water decomposes it, with formation of insoluble oxychloride or bismuthyl chloride, BiOCl, thus :

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

No pentachloride of bismuth is known. There are bromine, iodine, and fluorine analogues of the trichloride.

Bismuth Dioxide, Bi$_2$O$_2$, is a grayish-black powder, which burns when heated in air to the trioxide.

Bismuth Trioxide, Bi$_2$O$_3$, occurs as bismuth ochre. It is formed when the metal is burned in air, and by igniting the hydroxide or nitrate.

Bismuth Trihydroxide, Bi(OH)$_3$, separates when a solution of bismuth nitrate is dropped into a cold solution of potassium hydroxide. On drying at 100° it is converted into bismuthyl hydroxide, BiO.OH.

Bismuth Nitrate, Bi(NO$_3$)$_3$ or $\begin{matrix} NO_2-O \\ NO_2-O \\ NO_2-O \end{matrix} \Big\rangle Bi$.—This salt is prepared by dissolving the metal in nitric acid. The solution yields on evaporation hydrous crystals.

Basic Bismuth Nitrate, $\begin{matrix} NO_2-O \\ HO \\ HO \end{matrix} \Big\rangle Bi$.—This basic salt is ob-

tained as a curdy mass when bismuth nitrate is treated with cold water. If this remains in contact with the acid solution it is gradually converted into the salt $5Bi_2O_3.4N_2O_5 + 9H_2O$. On pouring a nitric acid solution of bismuth into water a basic salt separates, varying somewhat in composition according to the amount of water used in precipitating and washing. It has been long used in medicine, and is the most common preparation of bismuth.

Bismuth Sulphate, $Bi_2(SO_4)_3$, is said to remain when a solution of bismuth or its oxide in concentrated sulphuric acid is evaporated. The residue yields on treatment with water a basic salt, which loses water on heating, with formation of bismuthyl sulphate, $(BiO)_2SO_4$.

Bismuth Tetroxide, Bi_2O_4, Bismuth Pentoxide, Bi_2O_5, and Bismuthic Acid, $HBiO_3$, have been prepared.

Bismuth Trisulphide, Bi_2S_3, occurs as bismuthite. It can be prepared by melting together sulphur and bismuth, and also by precipitating a solution of bismuth with hydrogen sulphide. **Bismuth Disulphide, Bi_2S_2**, is known.

Vanadium, V.

Atomic Weight, 51.3.   *Density*, 5.5.

In 1801 Del Rio found a new element in a Mexican lead ore. Later, it was regarded as an impure chromium oxide. In 1830 Sefström discovered the same element in the ores of Taberg, and named it Vanadium, after Vanades, a Scandinavian goddess. Vanadium occurs very sparingly, though widely distributed, having been found in a number of clays and iron ores, and in trap and basalt. The metal is obtained with difficulty by reducing the dichloride at a red heat with hydrogen absolutely free from traces of oxygen. Metallic vanadium thus prepared is a light whitish-gray powder, which appears as a brilliant white crystalline mass under the microscope. It oxidizes slowly in the air, and does not decompose water at common temperatures. It burns brilliantly in the flame or when heated in oxygen. It does not fuse at a red heat in hydrogen. It is insoluble in hydrochloric acid and cold

sulphuric acid, whilst it dissolves quickly in nitric acid, forming a blue solution.

Vanadium Chlorides.—**Vanadium Tetrachloride, VCl_4,** is a brownish-red liquid, boiling at 154°, with partial decomposition. Its observed gas density is 96.7. **Vanadium Trichloride, VCl_3,** and **Vanadium Dichloride, VCl_2,** are formed when the foregoing compound is passed with hydrogen through a tube heated to dull redness. At a higher temperature they are reduced to the metal. No vanadium pentachloride is known.

Vanadium Oxychlorides.—**Vanadyl Trichloride, $VOCl_3$,** corresponds to phosphorus oxychloride. It is a lemon-yellow liquid, boiling at 126°.7, and having a gas density of 88.2. **Vanadyl Dichloride, $VOCl_2$, Vanadyl Monochloride, $VOCl$,** and **Divanadyl Monochloride, V_2O_2Cl,** are formed when vanadyl trichloride is reduced by hydrogen at a red heat.

No fluoride or oxyfluoride of vanadium is known, but a number of fluoxyvanadates have been prepared, one of which is $6NH_4F.V_2O_5.$ $2VOF_3 + 2H_2O$.

Vanadium Oxides are analogous to the oxides of nitrogen :

$$
\begin{array}{ll}
\text{Vanadium monoxide,} \ldots \ldots \ldots & V_2O \\
\text{Vanadium dioxide or hypovanadious oxide,} & V_2O_2 \\
\text{Vanadium trioxide or vanadious oxide,} \ldots & V_2O_3 \\
\text{Vanadium tetroxide or hypovanadic oxide,} & V_2O_4 \\
\text{Vanadium pentoxide or vanadic oxide,} \ldots & V_2O_5 \\
\end{array}
$$

No salts of vanadium monoxide have been prepared. All the others form salts with acids, and the two highest oxides are acid-forming oxides. The monoxide is formed by the slow oxidation of the metal, while the trioxide and tetroxide are produced by the partial reduction of the pentoxide.

Vanadium Dioxide, V_2O_2, may be obtained by reducing the higher oxides by potassium. It was regarded as metallic vanadium by Berzelius. It conducts electricity, and burns when heated in air to the trioxide. It is insoluble in acids, except aqua regia.

Vanadium Pentoxide, V_2O_5, is the most important of the vanadium oxides. It is obtained by roasting ammonium metavanadate, and in a purer state by decomposing vanadyl trichloride by water. Vanadium pentoxide is soluble in about 1000 parts of water, forming a tasteless yellow solution which turns blue litmus paper red. It is both a basic and an acidic oxide. With strong acids it forms salts of the trivalent radical vanadyl, VO.

Vanadyl Sulphate, $(VO)_2(SO_4)_3$, is obtained by dissolving the pentoxide in hot sulphuric acid.

Orthovanadic Acid, $VO(OH)_3$, is not known.

Divanadic Acid, $H_4V_2O_7$, has been prepared.

Metavanadic Acid, VO_2OH, is a yellow pigment known as vanadium bronze. It is obtained as brilliant golden scales by boiling copper vanadate with a solution of sulphurous acid.

The vanadates correspond to the phosphates. Sodium Metavanadate, $NaVO_3$; Sodium Orthovanadate, Na_3VO_4; Sodium Divanadate, $Na_4V_2O_7$; and more complex polyvanadates, have been described.

Ammonium Metavanadate, NH_4VO_3, is prepared by dissolving vanadium pentoxide in ammonia and evaporating the solution. It is insoluble in solution of ammonium chloride, and separates when solid ammonium chloride is left in a solution of sodium meta- or di-vanadate:

$$Na_4V_2O_7 + 4NH_4Cl = 2NH_4VO_3 + 2NH_3 + H_2O + 4NaCl.$$

Vanadium Nitrides.—Vanadium is one of the few elements which unite directly with nitrogen. The mononitride, VN, is formed when the metal is heated in nitrogen, and also when the oxide is heated in ammonia. Berzelius mistook the vanadium nitride for the metal. The dinitride, VN_2, is known.

Niobium, Nb.

Atomic Weight, 94. *Density*, 7.

Niobium is found in columbite and a few other rare minerals, and is usually associated with tantalum. The metal is obtained in the form of a steel-gray crust when the vapor of the chloride mixed with hydrogen is passed through a strongly heated tube. It ignites at a low temperature and burns brilliantly in air. The metal is soluble in sulphuric acid, but is only slightly attacked by aqua regia.

Niobium Trichloride, $NbCl_3$, is obtained by passing the vapor of the pentachloride through a heated tube. It is non-volatile, and is not decomposed by water. When heated in carbon dioxide, the oxychloride, $NbOCl_3$, results. This reaction is not exhibited by any other metallic chloride. (Roscoe.)

Niobium Pentachloride, $NbCl_5$, forms in yellow needles when chlorine gas is passed through a heated mixture of the pentoxide and charcoal. It fuses at 194°, and boils at 240°.5. Its observed gas density is 138°.6, the formula $NbCl_5$ requiring 135.3.

Niobium Oxychloride or Niobyl Chloride, $NbOCl_3$, is formed by the direct union of niobium dioxide with chlorine. Its observed gas density is 113, theory requiring 108.

Niobium Oxyfluoride, $NbOF_3$, has been prepared. The pentafluoride, NbF_5, is known only in combination, e.g., potassium niobium fluoride, $2KF.NbF_5$.

Niobium Dioxide, Nb_2O_2, is obtained by intensely heating a mixture of potassium oxyfluoride, $3KF.NbOF_3$, and sodium. It is an insoluble white powder, which burns brilliantly when heated in air.

Niobium Tetroxide, Nb_2O_4, is obtained in the form of a heavy black powder when the pentoxide is strongly ignited in hydrogen. It is insoluble in acids.

Niobium Pentoxide, Nb_2O_5, is prepared by heating potassium niobium fluoride with sulphuric acid, and dissolving out the potassium sulphate formed with water. The residue is then heated with ammonium carbonate to remove sulphuric acid. Thus obtained it is a white amorphous powder, which becomes denser and crystalline on ignition.

Niobium Hydroxide or Niobic Acid is formed when the pentachloride or oxychloride is decomposed by water. The product, dried at 100°, contains varying proportions of water. Niobic acid is soluble in alkali carbonates and hydroxides, and after treatment with hot hydrochloric acid is soluble in water.

Niobic acid forms complex poly-acid salts, of which the best known is potassium hexniobate, $K_8Nb_6O_{19} + 16H_2O$. This salt is formed when niobium pentoxide is fused with twice its weight of potassium carbonate.

Didymium, Di.

Atomic Weight, 145.   *Density*, 6.54.

This element occurs very sparingly, and is associated with cerium and lanthanum. Metallic didymium is obtained by the electrolysis of the chloride. It is ductile, has an almost white color, and tarnishes in air, and in the form of filings burns brilliantly in the flame. The didymium compounds closely resemble the lanthanum compounds, and in general present more analogy to the compounds of the third group than to those of the fifth. Its highest oxide, Di_2O_5, is the analogue of the highest oxides of the members of the fifth group.

Didymium Chloride, $DiCl_3 + 6H_2O$, crystallizes from a solution of the oxide in hydrochloric acid.

Didymium Sesquioxide, Di_2O_3, forms a white powder when the nitrate or oxalate is ignited. It is a strongly basic oxide, dissolving in dilute acids, and setting ammonia free from ammonium salts. It absorbs carbon dioxide from the air. In hot water it changes gradually to the hydroxide.

Potassium hydroxide precipitates the hydroxide $Di(OH)_3$ from a solution of the chloride.

Didymium Sulphate, $Di_2(SO_4)_3 + 8H_2O$, is converted by ignition at a red heat into $(DiO)_2SO_4$, the analogue of vanadyl and bismuthyl sulphates.

Didymium Pentoxide, Di_2O_5, results from the ignition of the nitrate (Bruner). It dissolves in dilute sulphuric or nitric acid, without evolution of gas, but in concentrated acids ozonized oxygen is set free. On adding a solution of potassium hydroxide to a solution of didymium nitrate and hydrogen dioxide, the hydroxide $DiO(OH)_3$ separates. This compound, analogous in formula to orthophosphoric acid, does not form salts with bases.

Samarium, Sm.

Atomic Weight, 150.

This very rare element was discovered by means of the spectroscope in 1879, by Lecoc de Boisbaudran, in the mineral samarskite. It has been found in a few other minerals. The metal has not been isolated. Samarium compounds resemble those of didymium, and, like the latter, samarium exhibits analogy to the elements of the third group.

Samarium Chloride, $SmCl_3 + 6H_2O$, forms large deliquescent crystals.

Samarium Hydroxide is white, gelatinous, and insoluble in alkalies. It is converted by ignition into the oxide Sm_2O_3. A higher oxide is precipitated when a solution of samarium and hydrogen dioxide is treated with ammonia. The precipitate loses oxygen readily, and after drying has the composition Sm_4O_9, or very nearly Sm_2O_5.

Samarium Sulphate, $Sm_2(SO_4)_3 + 8H_2O$, forms brilliant crystals. It does not form an alum, with alkali sulphates.

Tantalum, Ta.

Atomic Weight, 183.

Metallic tantalum apparently has not been prepared in the pure state. Berzelius, by heating potassium tantalum fluoride with potassium, obtained a black powder which burned to oxide when heated in air, and was insoluble in acids, excepting hydrofluoric. The tantalum compounds resemble those of niobium.

Tantalum Pentachloride, $TaCl_5$, is obtained by the same method as niobium pentachloride. It melts at 211°, and boils at 240°. Its observed gas density is 183.8, the formula $TaCl_5$ requiring 180.

Tantalum Pentafluoride, TaF_5, is known only in solution, or in combination with other fluorides, as for example, $2KF.TaF_5$.

Tantalum Tetroxide, Ta_2O_4, results from intense ignition of the pentoxide in a carbon crucible. It is very hard, insoluble in all acids, and when heated burns to the pentoxide.

Tantalum Pentoxide, Ta_2O_5, is obtained by the method described for the preparation of niobium pentoxide. It is insoluble in acids, and has a density of 7.35–8.

Tantalum Hydroxide or Tantalic Acid, $HTaO_3$, is obtained as a crystalline powder when tantalum pentachloride is decomposed by moist air, and the product treated with ammonia, and dried at 100°. It is soluble in hydrogen potassium oxalate, and hydrofluoric acid. It is converted into the pentoxide by ignition.

Tantalates.—Some native tantalates are normal salts of the above acid. Sodium and potassium salts of the unknown acid, $H_8Ta_6O_{19}$, and also other polytantalates, have been prepared.

Summary of the Fifth Group.

Hydrides and Halides.

Nitrogen, . . .	N_2H_4	NH_3		NCl_3	
Phosphorus, . .	P_2H_4	PH_3	PI_2	PCl_3	PCl_5
Arsenic, . . .		AsH_3	AsI_2	$AsCl_3$	AsI_5
Antimony, . .		SbH_3		$SbCl_3$	$SbCl_5$
Bismuth, . . .			$BiCl_2$	$BiCl_3$	
Vanadium, . .			VCl_2	VCl_3	VCl_4
Niobium, . . .				$NbCl_3$	$NbCl_5$

Didymium	$DiCl_3$		
Samarium	$SmCl_3$		
Tantalum, ...			$TaCl_5$

OXIDES.

Nitrogen, ...	N_2O	NO	N_2O_3	N_2O_4	N_2O_5
Phosphorus, ...			P_2O_3	P_2O_4	P_2O_5
Arsenic, ...			As_4O_6		As_2O_5
Antimony, ...			Sb_4O_6	Sb_2O_4	Sb_2O_5
Bismuth, ...		Bi_2O_2	Bi_2O_3	Bi_2O_4	Bi_2O_5
Vanadium, ...	V_2O	V_2O_2	V_2O_3	V_2O_4	V_2O_5
Niobium, ...		Nb_2O_2		Nb_2O_4	Nb_2O_5
Didymium			Di_2O_3		Di_2O_5
Samarium			Sm_2O_3		$Sm_2O_5?$
Tantalum, ...				Ta_2O_4	Ta_2O_5

HYDROXIDES.

Nitrogen, .	$NOH?$	$NO.OH$			$NO_2.OH$
Phosphorus, .		$P(OH)_3$	$PO(OH)_3$	$(PO)_2O(OH)_4$	$PO_2.OH$
Arsenic, . .		$As(OH)_3?$	$AsO(OH)_3$	$(AsO)_2O(OH)_4$	$AsO_2.OH$
Antimony, .		$Sb(OH)_3$	$SbO(OH)_3$	$(SbO)_2O(OH)_4$	$SbO_2.OH$
Bismuth, . .		$Bi(OH)_3$			$BiO_2.OH$
Vanadium, .				$(VO)_2O(OH)_4$	$VO_2.OH$
Niobium, .		Composition of hydroxide unknown.			
Didymium .		$Di(OH)_3$	$DiO(OH)_3$		
Samarium .		Composition of hydroxides unknown.			
Tantalum, .					$TaO_2.OH$

The distinguishing characteristics of the fifth group are exhibited in the pentoxides, which are all acid anhydrides, excepting those of didymium and samarium, and in the acid hydroxides, of which nitric acid, $NO_2.OH$, is the first member. No other group of elements forms similar classes of compounds. The trichlorides and trioxides indicate a close relationship in chemical properties, but are not characteristic of the fifth group, showing rather an analogy in formula to the trichlorides and oxides of the third group, of which $AlCl_3$ and Al_2O_3 are examples.

The hydrides, NH_3, PH_3, AsH_3, and SbH_3, exhibit a gradation of properties with increasing atomic weights. Nitrogen, with

the lowest atomic weight, forms with hydrogen a stable basic compound; phosphine, PH_3, is less stable and but feebly basic; while arsine, AsH_3, and stibine, SbH_3, are still less stable, and do not combine with acids.

Nitrogen stands apart from all the other members of the group in many properties. This is seen in ammonia, and in the nitrogen halides, which are highly explosive, and do not react with water to form oxides or hydroxides as do the tri- and pentachlorides of the other elements of the group, $VaCl_3$ excepted. Nitrogen and phosphorus do not form basic oxides and hydroxides, and there are no salts in which these elements are basic radicals. Arsenic, antimony, and bismuth form salts with oxygen acids, and thus exhibit basic characters. Their sulphates are $As_2(SO_4)_3 + SO_3$, $Sb_2(SO_4)_3$, $Bi_2(SO_4)_3$. They are decomposed by water into basic salts. Vanadium, on the other hand, forms vanadyl sulphate, $(VO)_2(SO_4)_3$, while well-defined sulphates of niobium and tantalum are unknown.

The densities of the elements of the fifth group increase with their atomic weights. Nitrogen and phosphorus, like other non-metals, have low densities. Their melting and boiling points are widely separated from the melting and boiling points of the remaining members of the group. Nitrogen and, to a less degree, phosphorus stand apart in physical as well as in chemical properties.

	Atomic Weight.	Density.	Gas Density.	Melting Point.	Boiling Point.
Nitrogen, . . .	14	0.88 (liquid)	14	$-214°$	$-194°$
Phosphorus, . .	31	1.83	62	44°	278°
Vanadium, . .	51.3	5.5	—	above red heat.	——
Arsenic, . . .	75	5.7	150	dull red.	——
Niobium, . . .	94	7	—	above red heat.	——
Antimony, . .	120	6.7	—	425°	——
Didymium, . .	145	6.5	—	——	——
Samarium, . .	150	——	—	——	——
Tantalum, . .	183	——	—	——	——
Bismuth, . . .	208	9.8	—	270°	——

THE THIRD GROUP.

The members of this group are boron and aluminum, and the rare elements gallium, indium, thallium, scandium, yttrium, lanthanum, erbium, and ytterbium.

They are all trivalent elements, although thallium is univalent in thallous compounds, and boron pentavalent in a few compounds.

Boron, B.

Atomic Weight, 11.   *Density,* 2.7.

This element is found in native borates and a few other minerals. In order to obtain free boron a mixture of boric oxide and sodium is intensely heated under a layer of common salt, and the molten mass is poured into dilute hydrochloric acid. The sodium chloride, sodium borate, and boric oxide dissolve, and the boron remains as an amorphous brown powder. Amorphous boron does not oxidize at common temperatures, but burns brilliantly to boric oxide when heated in air. It dissolves in molten aluminum, and when the mass cools brownish-yellow crystals form. These may be separated by dissolving the aluminum in hydrochloric acid or a solution of sodium hydroxide, and further purified by treatment with a mixture of nitric and hydrofluoric acids. The crystals are not pure boron, but contain a little aluminum, the proportion of the two elements varying in different preparations. The analysis of one sample corresponded to the formula AlB_{12}, and of another to AlB_{23}. Pure crystalline boron does not appear to

have been obtained. The above-described crystals are, however, regarded as a modification of boron. They have a brilliant lustre, are almost as hard as the diamond, and will scratch corundum. They are insoluble in acids, but are acted on by molten sodium hydroxide, with formation of sodium borate. In the preparation of crystalline boron, graphite-like scales, of the composition AlB_2, have occasionally been obtained. These were formerly regarded as a third modification of boron.

Boron Hydride, BH_3?—When magnesium dust is fused with boric oxide an impure magnesium boride is formed. This yields on treating with hydrochloric acid a gas which is mostly hydrogen, but which contains a volatile boron compound, probably having the composition BH_3.

Boron Fluoride, BF_3 or $B{\overset{\displaystyle F}{\underset{\displaystyle F}{\diagup}}}{-}F$.—This compound is easily obtained by the

following reaction :

$$3Ca{<}^{F}_{F} + {\overset{B=O}{\underset{B=O}{>O}}} + 3SO_2{<}^{OH}_{OH} = 3SO_2{<}^{O}_{O}{>}Ca + 3H_2O + 2B{\overset{\displaystyle F}{\underset{\displaystyle F}{\diagdown}}}{-}F.$$

It is a colorless suffocating gas, having a density corresponding to its formula. It unites with ammonia to form a white compound having the composition $BF_3.NH_3$. This body is dissociated by heat into a mixture of the gases BF_3 and NH_3, which combine again on cooling.

Boron Chloride, BCl_3 or $B{\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\diagup}}}{-}Cl$, is formed by the direct

union of its elements, and also by heating a mixture of boric oxide and charcoal in chlorine. It is a colorless liquid, boiling at 17°. Its gas density corresponds to its formula. It fumes in moist air, and is decomposed by water into hydrochloric and boric acids. BBr_3 is known, but the iodide has not been obtained.

Boron Oxychloride, $BOCl_3$ or $O = B {<}^{Cl}_{\phantom{<}Cl}_{Cl}$ —This substance

has been obtained as a yellowish green liquid in the preparation of boron chloride. It is unchanged at 100°, but decomposes at higher temperatures as follows :

$$3BOCl_3 = B_2O_3 + BCl_3 + 3Cl_2.$$

It is decomposed slowly by water into boric and hydrochloric acids and free chlorine. This oxychloride is of theoretical interest, as it indicates a pentavalent character in boron.

Boric Oxide, Boric Anhydride, B_2O_3 or $^{B\,=\,O}_{B\,=\,O} {>} O.$ —This is the

only known oxide of boron. It is easily obtained by heating boric acid until the mass is in a quiet state of fusion. On cooling it cracks spontaneously. It is soluble in water, and becomes opaque in moist air. At high temperatures boric oxide decomposes salts of acids more volatile than itself.

Boric or Orthoboric Acid, H_3BO_3 or $B {<}^{OH}_{\phantom{<}OH}_{OH}$ —This acid is

formed from boric oxide and water, thus :

$$^{B\,=\,O}_{B\,=\,O} {>} O + 3H_2O = 2B {<}^{OH}_{\phantom{<}OH}_{OH}.$$

It occurs in volcanic regions in the jets of steam which issue from the vents about the volcanoes. Tuscany has supplied the European market with boric acid. It is also obtained from native borates. It is soluble in three parts of water at 100°, and in about 25 parts at ordinary temperatures. When its solution is boiled, a little of the acid passes off with the steam—a fact which explains the presence of boric acid in

volcanic vapors. Alcoholic vapors also carry it, and burn with a characteristic green flame. If a piece of turmeric paper is moistened with a solution of boric acid and then dried, a peculiar red coloration appears, which differs from the alkaline reaction of turmeric paper in that it is not changed to yellow by dilute hydrochloric acid.

Exp. 184.—*a.* Place in a test-tube 10 cc. of cold water and 1 cc. of concentrated sulphuric acid, heat to boiling, and add 5 grams of borax. After the latter has dissolved, allow the solution to cool. Pour off the liquid as completely as possible, and wash the crystals twice with a little water. The boric acid obtained will not be free from sulphuric acid and sodium sulphate, but will answer for further experiments. Represent by an equation the reaction by which the boric acid is formed.

b. Dissolve a little boric acid in water in a test-tube, boil the solution, and hold a Bunsen flame over the escaping vapor. The greenish tinge of the gas flame is due to boric acid in the steam.

c. Dissolve some boric acid in a small porcelain dish in a tablespoonful of ethyl alcohol, or better, impure methyl alcohol of commerce. Warm gently and ignite the alcohol.

Metaboric Acid, HBO$_2$ or O$=$BO–H, is formed from orthoboric acid by the removal of one molecule of water :

$$\frac{HO}{HO}{>}B\text{–}OH \,=\, O{=}B\text{–}OH + H_2O.$$

It remains as a white powder when orthoboric acid is heated to 100°. At this temperature, according to Schaffgotsch, it volatilizes slowly but completely.

Tetraboric Acid, B$_4$O$_5$(OH)$_2$, is a brittle mass attained by prolonged heating of metaboric acid to 160°. It may be viewed as a derivative of the ortho-acid, thus :

$$4\,H_3BO_3 = B_4O_5(OH)_2 + 5H_2O, \text{ or}$$

$$
\begin{aligned}
&\text{B} \Big\langle\begin{array}{l}\text{OH}\\\text{OH}\\\text{OH}\end{array} \\
&\text{B} \Big\langle\begin{array}{l}\text{OH}\\\text{OH}\\\text{OH}\end{array} \quad = \\
&\text{B} \Big\langle\begin{array}{l}\text{OH}\\\text{OH}\\\text{OH}\end{array} \\
&\text{B} \Big\langle\begin{array}{l}\text{OH}\\\text{OH}\\\text{OH}\end{array} \\
&\text{B} \Big\langle\begin{array}{l}\text{OH}\\\text{OH}\\\text{OH}\end{array}
\end{aligned}
\qquad
\begin{aligned}
&\text{B} \Big\langle\begin{array}{l}\text{OH}\\\end{array}\\
&O\Big\langle\quad\Big\rangle O\\
&\text{B}\\
&\qquad\Big\rangle O + 5H_2O.\\
&\text{B}\\
&O\Big\langle\quad\Big\rangle O\\
&\text{B} \Big\langle\begin{array}{l}\\\text{OH}\end{array}
\end{aligned}
$$

Borax, Sodium Tetraborate, $Na_2B_4O_7 + 10H_2O$.—Borax is the most important salt of boric acid. It occurs in crystals in California, Peru, and in various localities in Asia. Borax is found in abundance in some salt lakes. A considerable portion of the borax of commerce is manufactured from boric acid by treatment with sodium carbonate. The pentahydrated salt $Na_2B_4O_7 + 5H_2O$ separates in octahedral crystals, when a hot saturated solution cools; after the temperature falls to 56° large monoclinic prisms of the decahydrated salt are deposited. Both hydrates are sold under the name of borax. The decahydrated salt dissolves in 14 parts of water at ordinary temperature, and in half its weight in water at 100°. Borax has a slightly alkaline taste and reaction. It appears to separate into boric acid and sodium hydroxide when dissolved in a large quantity of water. If, for example, to a concentrated solution of borax containing litmus acetic acid is added until a faint red tint appears, and then much water is added, the blue color of litmus is seen. The cleansing action of a solution of borax is due in part to the free alkali it contains.

Both the octahedral and prismatic borax swell when heated, give off water, and are converted into a white

porous mass of anhydrous borax, $Na_2B_4O_7$, which melts at a high temperature, forming borax glass. Molten borax possesses the property of dissolving metallic oxides, many of which give characteristic colors to the flux. Hence the use of borax in blowpipe tests. Borax is used in soldering gold, silver, and copper, and in welding iron, to cleanse the surfaces of the metals.

Exp. 185.—Add to a concentrated solution of borax a little litmus solution and acetic acid to faint acid reaction, then dilute the solution largely with water.

Exp. 186.—Heat a small ring on the end of a copper wire above the lamp flame until a coating of oxide forms, and fuse on it a little borax, taking care to heat in the upper and oxidizing part of the flame. The copper oxide will dissolve and color the borax glass green, leaving the surface of the copper bright.

Sodium Metaborate, BO–O–Na, is obtained by fusing together equivalent weights of borax and of sodium carbonate. It crystallizes with 4 molecules of water. The salt dry and in solution, absorbs carbon dioxide with formation of sodium carbonate and sodium tetraborate.

Sodium Orthoborate, $B\begin{matrix}\diagup O-Na\\\leftarrow O-Na\\\diagdown O-Na\end{matrix}$—This salt is formed when boric oxide is fused with an excess of sodium hydroxide. It is converted by water into the metaborate.

Aluminum, Al.

Atomic Weight, 27. *Density,* 2.6.

Aluminum is the most abundant of the elements excepting oxygen and silicon. It is a constituent of soils, most rocks, and

many minerals. The metal is obtained from its chloride by electrolysis or by fusion with sodium. It is manufactured by melting together a double chloride of aluminum and sodium, metallic sodium and cryolite. The last is added as a flux.

Aluminum is not reduced from its oxide by carbon or hydrogen at the highest temperature of a wind furnace. Aluminum oxide, mixed with charcoal, is however reduced at the temperature of the voltaic arc, the metal at the same time volatilizing. When the reduction is made in the electrical furnace part of the vapor condenses in the layer of charcoal and part escapes from the furnace with the gases. If, however, the reduction is made in the presence of iron or copper these metals retain the aluminum, forming alloys of great industrial importance.

Pure aluminum is almost as white as tin, is capable of a good polish, and does not oxidize in air. The impure metal of commerce, containing small quantities of iron and silicon, soon tarnishes owing to formation of a thin coating of oxide. Aluminum is ductile, and very malleable. It melts at about 700°. The cast metal is about as hard as silver, but the hammered metal has the hardness of soft iron. Aluminum does not burn in air or oxygen except in the form of filings, thin foil, or fine wire. It dissolves in hydrochloric and sulphuric acids, and in solutions of the fixed alkalies. Nitric acid, concentrated or dilute, does not act on it. Organic acids have little action, but if common salt is present the metal slowly dissolves—a fact which precludes its use in culinary articles.

It is said that aluminum may be soldered by an alloy consisting of 5 parts of tin and 1 of aluminum. The metal on account of its lightness and great tensile strength is valuable for many purposes, but the high cost prevents the extensive use of it.

Aluminum bronze is an alloy of copper containing about 10 per cent of aluminum. It has the color of gold, is malleable, makes good castings, and is remarkable for its strength and

permanence in air. An increase of 2 or 3 per cent of aluminum renders the alloy brittle, and with increasing proportions of aluminum the color of the alloy becomes lighter.

Iron takes up several per cent of aluminum, but not as much as copper. The alloy of iron and aluminum is added to molten iron, the presence of a fraction of a per cent of aluminum having been found to greatly improve the quality of castings for various purposes.

Valence of Aluminum.—The gas density of aluminum chloride has been found at 350° to 440° to be 133.4 ; theory requires for Al_2Cl_6 128.2. The gas densities of the bromide and iodide correspond to the molecules Al_2Br_6 and Al_2I_6. These results have led to the view that the double atom Al_2 is tetra-valent, having the constitution $\begin{array}{c} Al\!\!\!<\!\!\!\equiv \\ | \\ Al\!\!\!<\!\!\!\equiv \end{array}$, and that aluminum is tetravalent. Recently (1887) Nilson has, however, found that the density of aluminum chloride diminishes at temperatures above 440°, and at 835° to 943° is 65.7 ; calculated for $AlCl_3$, 66.7. Aluminum is therefore trivalent.

Aluminum Chloride, $AlCl_3$ or $Al\!\!<\!\!\begin{array}{c} Cl \\ -Cl \\ Cl \end{array}$.—A solution of aluminum chloride is obtained by dissolving aluminum hydroxide in hydrochloric acid. If the solution is evaporated at ordinary temperature, crystals of $AlCl_3 + 6H_2O$ separate. These on heating lose hydrochloric acid and water, with the formation of alumina. The anhydrous aluminum chloride may be prepared by passing dry chlorine over the hot metal. The chloride volatilizes as fast as formed, thus constantly exposing a fresh surface of the metal to the gas. The chloride is made on a manufacturing scale by passing chlorine over a heated mixture of alumina and carbon :

$$\begin{matrix} Al=O \\ >O \\ Al=O \end{matrix} + 3C + 6Cl = 2Al{<}\begin{matrix} Cl \\ Cl \\ Cl \end{matrix} + 3CO.$$

The aluminum chloride distils and condenses in a suitable chamber. Common salt is often added to the mixture for the purpose of obtaining the double salt $NaCl.AlCl_3$, which is also volatile. Sodium aluminum chloride is more permanent in air than aluminum chloride, and hence is better adapted for use in the manufacture of the metal.

Aluminum Sodium Fluoride, $AlF_3.3NaF$, occurs abundantly as the mineral cryolite in Greenland. It is extensively used in the manufacture of aluminum compounds and sodium hydroxide.

Aluminum Oxide, Alumina, Al_2O_3 or $O=Al-O-Al=O$, occurs as the mineral corundum, of which the ruby, sapphire, oriental topaz, and oriental amethyst are varieties. *Emery* is granular gray or black corundum mixed with magnetite. Corundum ranks next to the diamond in hardness, hence its value in polishing and cutting. Aluminum oxide is prepared by igniting the hydroxide or aluminum salts of volatile acids. The artificial oxide dissolves with difficulty in acids, but may be rendered soluble by fusion with acid potassium sulphate or potassium hydroxide.

Aluminum Hydroxides.—Ammonia produces in solutions of aluminum salts a bulky gelatinous precipitate, which consists of $Al(OH)_3$ together with some water, and which, on drying at common temperature, corresponds to $Al(OH)_3 + H_2O$. This loses water on heating above 300°, and aluminum oxyhydroxide, $AlO.OH$, remains, which has the composition of the mineral diaspore. Precipitated aluminum hydroxide has the property of withdrawing dyestuffs and many salts from solutions. This property is applied in mordanting fabrics.

Exp. 187.—Make a cochineal solution by digesting some powdered cochineal insects in hot water. Filter, and add a solution of alum, and then ammonia, and collect the precipitate on a filter. If sufficient alum is used the carmine color will be completely removed from the solution.

Exp. 188.—Dip a piece of white cotton cloth into a dilute solution of alum, then into water containing a little ammonia. Make a logwood solution by boiling some logwood chips in water, and place in it the cloth impregnated with aluminum hydroxide, and also a piece of white cotton cloth which has not been mordanted. Boil the solution some minutes and then wash and dry the pieces.

A soluble aluminum hydroxide has been obtained by decomposing aluminum acetate by long heating with water. The solution on evaporation yields a gelatinous residue which when dried at 100° corresponds to $Al_2O(OH)_4$. Graham dialyzed a solution of basic chloride and obtained a neutral solution of alumina, which after some days changed to a jelly. The addition of traces of salts, acids, and alkalies coagulate both these soluble hydroxides.

Aluminates.—Aluminum hydroxide dissolves in solutions of the caustic alkalies with formation of compounds known as aluminates, in which aluminum acts as an acid radical.

Sodium Orthoaluminate, Na_3AlO_3 or $Al{\Large\langle}{\small\begin{matrix} O-Na \\ O-Na \\ O-Na \end{matrix}}$.— Aluminum dissolves in a solution of sodium hydroxide, and for each atom of metal dissolved three atoms of hydrogen are liberated, thus:

$$Al + 3Na-OH = Al{\Large\langle}{\small\begin{matrix} O-Na \\ O-Na \\ O-Na \end{matrix}} + 3H.$$

The orthoaluminate is said to separate when a solution of aluminum hydroxide in excess of sodium hydroxide is evaporated.

Sodium Metaluminate, $NaAlO_2$ or $O{=}Al-O-Na$.—This compound is made by fusing cryolite with lime, and by melting to-

gether a native aluminum hydroxide with sodium hydroxide. The mass in either case is lixiviated with water; the solution on evaporation yields the sodium aluminate as a white amorphous powder. Sodium aluminate is used in mordanting fabrics, and for the preparation of alumina.

The solution of sodium aluminate is decomposed by carbon dioxide with separation of aluminum hydroxide:

$$2 \, O{=}Al{-}O{-}Na + CO_2 + 3H_2O = 2Al{\Big\langle}{\overset{OH}{\underset{OH}{-}OH}} + CO{\Big\langle}{\overset{O{-}Na}{O{-}Na}}.$$

Calcium hydroxide precipitates calcium aluminate:

$$2 \, O{=}Al{-}O{-}Na + Ca{\Big\langle}{\overset{OH}{OH}} = {\overset{O{=}Al{-}O}{O{=}Al{-}O}}{\Big\rangle}Ca + 2Na{-}OH.$$

The strontium and barium aluminates are soluble in water. The potassium compound $2 \, O{=}Al{-}O{-}K + 3H_2O$ has been obtained in crystals.

Exp. 189.—Add sodium hydroxide cautiously to an alum solution until the precipitate which at first forms dissolves. Pass into the solution obtained carbon dioxide, or treat a solution of commercial sodium aluminate with carbon dioxide. Express the reactions by equations.

Aluminum Sulphate, $Al_2(SO_4)_3$ or
$$SO_2{\Big\langle}{\overset{O}{O}}{\searrow}Al \atop SO_2{\Big\langle}{\overset{O}{O}} \atop SO_2{\Big\langle}{\overset{O}{O}}{\nearrow}Al$$
.—This salt

is prepared by dissolving aluminum hydroxide in sulphuric acid, and also from clay. The clay, as free as possible from iron, is roasted to render the iron present less soluble, and the aluminum silicate more easily decomposed by the acid. It is then heated with sulphuric acid, and the solution, after the silica and undecomposed clay have subsided, is drawn off and

evaporated until it solidifies on cooling. This crude sulphate is used by dyers as a mordant. It is also used for " weighting paper."

Aluminum sulphate crystallizes with 16 molecules of water in pearly scales, but if ferric sulphate is present it is hygroscopic and contains rather more than 18 molecules of water. Freshly precipitated aluminum hydroxide dissolves in a solution of aluminum sulphate, with the formation doubtless of basic sulphate.

Alums.—Aluminum sulphate forms with alkali sulphates double salts which crystallize in octahedrons, usually exhibiting cubic faces. The name alum was formerly applied only to the potassium aluminum sulphate, but the term is now used to designate a group of analogous bodies, in which aluminum is replaced by iron, chromium, and other metals, and the potassium by other alkali metals, or by silver, thallium, or ammonium.

Potassium Alum, $Al_2(SO_4)_3.K_2SO_4 + 24H_2O$.—If a solution of aluminum sulphate is mixed with a solution of potassium sulphate in sufficient quantity to form the double salt, no change in temperature will occur—an indication that there has been no combination. The solution of the two salts, however, yields on evaporation crystals of alum.

At 0° 100 parts of water dissolve 3.9, at 20° 15, and at 100° 357.5 parts of $Al_2(SO_4)_3.K_2SO_4 + 24H_2O$. Alum melts at 92° in its water of crystallization, most of which it loses slowly at 100°, and the last portions on gentle ignition. The porous mass thus obtained, known as burnt alum, dissolves slowly in water. If potassium hydroxide is slowly added to potash alum, so long as the precipitate redissolves readily on stirring, a neutral solution is obtained, which is known in the arts as neutral alum. Solutions of common alum, to which a small quantity of neutral alum has been added, yield

on spontaneous evaporation cubic crystals of the same composition as octahedral alum.

Ammonium Alum, $Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 24H_2O$, has been manufactured at times when ammonium sulphate has been cheaper than potassium sulphate. It is somewhat more soluble in water than potassium alum, which it closely resembles. Commercial alum sometimes contains both potassium and ammonium. Alum is valuable as a source of aluminum hydroxide free from iron, but it is largely replaced for use in dyeing by aluminum sulphate and sodium aluminate.

Exp. 190. —Take 20 grams crystallized aluminum sulphate and the weight of ammonium sulphate required to form ammonium alum. Dissolve the two salts together in 100° cc. of boiling water, filter the solution into a porcelain dish, and let stand for several days to crystallize. Test one of the crystals for ammonia and also for aluminum.

Gallium, Ga.

Atomic Weight, 70.   Density, 5.9.

Gallium was discovered by means of the spectroscope in 1875 by Lecoq de Boisbaudran in zinc blende from the mine of Pierrefitte in the Pyrenees. The blende of Bensberg has since proved to be a better source of the metal, and from 43,000 kilos. of the ore 62 grams of gallium were obtained. The metal is separated by electrolyzing a solution of a salt of it in potassium hydroxide.

Gallium melts at 30° to a brilliant white liquid, which may be cooled 10°-15° below its fusing point without solidifying. In the solid state the metal has a bluish tinge, is hard, and but slightly malleable. It does not lose its lustre in air or in water free from air, but slowly tarnishes in ordinary water. It oxidizes superficially at a red heat in the air, and does not volatilize. Cold nitric acid is without action on the metal, but the hot acid dissolves it slowly. Hydrochloric acid dissolves it readily and potassium hydroxide slowly with evolution of hydrogen.

Gallium Dichloride, GaCl₂.—Gallium is readily attacked by chlorine with formation of gallium dichloride if the metal is in excess and the current of chlorine moderate. With an excess of chlorine the trichloride, GaCl₃, is formed. The latter is the more volatile of the two compounds. Gallium dichloride is decomposed by water with evolution of hydrogen and formation of the trichloride.

Gallium Trichloride, GaCl₃, fumes strongly in the air and quickly deliquesces. It fuses at 75°.5 and boils at 215°–220°. Its gas density at 273° is 171.8, corresponding to gas molecules of Ga₂Cl₆. At high temperatures the density found equals 95.3, showing dissociation into molecules of GaCl₃. At still higher temperatures it decomposes.

Gallium Oxide, Ga₂O₃, is obtained by igniting the nitrate. Ammonia added to a solution of a gallium salt precipitates gallium oxide (hydroxide?), and the precipitate is more soluble in ammonia than aluminum hydroxide. Potassium hydroxide also precipitates the oxide, which readily dissolves in an excess of the precipitant. From this alkaline solution carbonic acid again precipitates the oxide

Gallium Nitrate, Ga(NO₃)₃, is obtained by evaporating at 40° a solution of gallium in nitric acid.

Gallium Sulphate, Ga₂(SO₄)₃, is very soluble in water, and forms with ammonium sulphate gallium-ammonium alum, which crystallizes in octahedrons or octahedrons with cubic facets.

Indium, In.

Atomic Weight, 113.7. *Density,* 7.4.

Indium occurs in small quantities in the zinc blende of various localities. It was discovered by means of the spectroscope in 1863 by Reich and Richter in the blende of Freiberg, Saxony, which contains about 0.1 per cent of indium.

Indium is a silver-white non-crystalline metal, softer than lead. It melts at 176° and oxidizes at a higher temperature. At a red heat it burns with a blue flame to the oxide. It is less volatile than zinc and cadmium, and is not corroded by moist air or boiling water. It dissolves slowly in dilute hydrochloric and sulphuric acids, and readily in nitric acid.

Indium Chloride, InCl₃, is prepared by burning the metal in chlorine. It is very deliquescent.

The observed gas density of indium chloride is 113.6; theory requires 109.9 for $InCl_3$.

Indium Oxide, In_2O_3, is obtained by ignition of the nitrate, and also by burning the metal. It is a pale-yellow powder, which turns brown on heating.

Indium Hydroxide, $In(OH)_3$.—Ammonia produces in solutions of indium salts a bulky precipitate similar to aluminum hydroxide. It has the composition of $In(OH)_3$ after drying at 100°. It is soluble in acids. Potassium and sodium hydroxides dissolve it, but the solution soon becomes turbid owing to separation of indium hydroxide.

Indium Sulphate, $In_2(SO_4)_3$, is obtained by dissolving the oxide in sulphuric acid. With ammonium sulphate it forms the alum $In_2(SO_4)_3$. $(NH_4)_2SO_4 + 24H_2O$.

Thallium, Tl.

Atomic Weight, 204. *Density,* 11.8.

Thallium is widely distributed, although found only in small quantities. It occurs in copper and iron pyrites and other sulphides of many localities, and has been found in some spring waters. Thallium is best obtained from dust which collects in the flues to the chambers in which thalliferous pyrites is burned in the manufacture of sulphuric acid. The dust seldom contains more than a fraction of one per cent of the metal.

Thallium was discovered by Crookes in a seleniferous deposit from a sulphuric-acid factory in the Harz. From this deposit selenium was prepared. This left on distilling a residue that gave in the spectroscope a single green line hitherto unknown.

Metallic thallium is separated from its solutions by zinc or by electrolysis, and also by fusing the iodide with potassium cyanide. It is not quite as white as silver, is softer than lead, melts at 290°, and may be distilled at a white heat in hydrogen. The bright metal tarnishes quickly in air, becoming covered with a thin film of thallous oxide, which protects it from further oxidation.

Thallium forms two series of compounds : the thallous, in which it is univalent; and the thallic compounds, in which it is trivalent. In thallous compounds thallium presents close analogy in properties to the alkali metals and to silver.

Thallous Compounds.

Thallous Chloride, TlCl, forms a white precipitate when hydrochloric acid is added to a solution of a thallous salt. It dissolves in 63 parts of water at 100° and in 504 parts at 0°. It crystallizes in cubes from hot solutions. Two determinations of its gas density gave 106.8 and 126 ; TlCl requires 119.

Thallous Iodide, TlI, is very insoluble in water, and thallium may be separated as iodide from dilute solutions by addition of potassium iodide.

Thallous Oxide, Tl$_2$O or Tl–O–Tl, is obtained by heating thallous hydroxide to 100° out of contact with air. It is a black powder, which absorbs moisture from air, and dissolves in water with formation of the hydroxide.

Thallous Hydroxide, Tl–OH, is best prepared by decomposing a solution of thallous sulphate with barium hydroxide. The solution filtered from the barium sulphate yields on evaporation yellow crystals, having the composition TlOH + H$_2$O. The solution of thallous hydroxide has a strong alkaline reaction, and is similar to potassium hydroxide in its deportment towards solutions of metallic salts.

Thallous Nitrate, TlNO$_3$ or NO$_2$–O–Tl, is formed together with a little thallic nitrate when thallium is dissolved in nitric acid. It is a soluble salt, which melts without decomposition at 205°.

Thallous Sulphate, Tl_2SO_4 or $SO_2 < {}^{O-Tl}_{O-Tl}$.—This salt is obtained by dissolving the metal or thallous hydroxide in sulphuric acid. It crystallizes in rhombic prisms, isomorphous with potassium sulphate. With aluminum sulphate it forms the alum $Al_2(SO_4)_3 . Tl_2SO_4 + 24H_2O$. Hydrogen thallous sulphate, $HTlSO_4$, has been prepared.

Thallous Sulphide, Tl_2S, separates as a black precipitate when an alkaline solution of a thallous salt is treated with hydrogen sulphide.

Thallic Compounds.

Thallic Oxide, Tl_2O_3, is formed when thallium burns in oxygen and when thallic hydroxide is heated to $100°$–$115°$. It gives off oxygen at a strong red heat, and is insoluble in water and in caustic alkalies. It dissolves in warm sulphuric acid with evolution of oxygen.

Thallic Hydroxide.—Ammonia and potassium hydroxide produce in a solution of thallic chloride a precipitate which on drying has the composition $TlO . OH$ ($= O = Tl–OH$).

Thallic Chloride, $TlCl_3$ or $Tl {<}^{Cl}_{Cl}{\,}^{Cl}$.—This compound is formed when thallic hydroxide is dissolved in cold hydrochloric acid, or by treating thallium or thallous chloride under water with chlorine. The solution on evaporation in vacuum yields hydrous crystals, which become anhydrous at $50°$–$60°$, and at $100°$ lose chlorine.

Thallic Sulphate, $Tl_2(SO_4)_3 + 7H_2O$ or

$$SO_2 <_{O}^{O} >Tl$$
$$SO_2 <_{O}^{O}$$
$$SO_2 <_{O}^{O} >Tl$$

$+ 7H_2O.$

—This salt separates in crystals when a solution of thallic hydroxide in sulphuric acid is evaporated. The salt is decomposed by water with separation of thallic hydroxide.

Thallic Nitrate, $Tl(NO_3)_3$ or

$$NO_2-O$$
$$NO_2-O >Tl,$$
$$NO_2-O$$
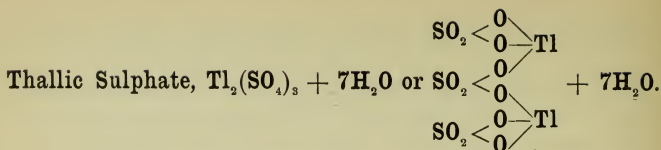
separates in hydrous deliquescent crystals from a solution of the hydroxide in nitric acid of density 1.40. They decompose on heating with water.

Scandium, Sc.

Atomic Weight, 44.

This element was discovered by Nilson in 1879 in his attempt to purify ytterbium oxide, which was obtained mostly from the minerals gadolinite and euxenite. After repeating a number of times a process for separating the oxides of erbium and ytterbium, he finally obtained a small residue of earthy oxide, which he found to possess a lower combining weight than the oxides of erbium and ytterbium. This residue was submitted to Thalen, who found in addition to the spectra of erbium and ytterbium a number of lines of the new element.

Scandium Oxide, Sc_2O_3, is a white, light, infusible powder, in appearance much like magnesia. It is obtained by the ignition of the hydroxide, nitrate, or sulphate. It dissolves in boiling concentrated nitric or hydrochloric acid. Addition of ammonia to a solution of a scandium salt precipitates scandium hydroxide, which is insoluble in caustic alkalies.

Scandium Nitrate crystallizes from solutions of the salt which have been evaporated to syrupy consistence. It gives off nitric acid on heating, and a basic salt is formed which is completely soluble in water. If the decomposition is carried so far that only a little nitric acid remains, the residue renders water milky, and the water does not

become clear even on long standing. Nilson regards this as character-
istic of scandium.

Scandium Sulphate, $Sc_2(SO_4)_3$, is prepared by heating the nitrate with
sulphuric acid. It crystallizes from aqueous solutions with six molecules
of water. The scandium potassium sulphate, $Sc_2K_6(SO_4)_6$, is insoluble
in a saturated solution of potassium sulphate.

Yttrium, Y.

Atomic Weight, 89.

Yttrium has not been separated in the pure state.

Yttrium Oxide, Y_2O_3, is a yellowish-white powder prepared by igniting
the oxalate or hydroxide. It does not unite directly with water, but
the hydroxide is obtained as a gelatinous precipitate when a caustic
alkali is added to a solution of an yttrium salt. The hydroxide decom-
poses ammonium salts, and like the alkalies combines directly with
carbon dioxide.

Yttrium Chloride, YCl_3.—Yttrium oxide dissolves slowly in hydro-
chloric acid, and the solution on evaporation yields crystals of the com-
pound $YCl_3 + 6H_2O$, which becomes anhydrous when ignited with
ammonium chloride.

Yttrium Nitrate, $Y(NO_3)_3 + 6H_2O$, forms needle-shaped crystals which
do not change in air.

Yttrium Sulphate, $Y_2(SO_4)_3 + 8H_2O$.—This salt is more soluble in cold
than in warm water. 100 parts of water at 15°.5 dissolve 15.2 parts of
the anhydrous salt, but on warming a portion of the salt crystallizes
out.

Alums do not appear to have been obtained with yttrium sulphate,
but double salts have been prepared with potassium and ammonium
sulphates.

Lanthanum, La.

Atomic Weight, 139.   Density, 6.1.

Lanthanum has been found in a few minerals associated with cerium
and didymium. The metal was obtained by Hildebrand and Norton

by electrolyzing lanthanum chloride. It is readily acted on by strong nitric acid, and tarnishes quickly in dry air. It is malleable, but cannot be drawn into wire. The finely divided metal burns brilliantly in air. It decomposes water with evolution of hydrogen and formation of lanthanum hydroxide.

Lanthanum Oxide, La_2O_3, is obtained by igniting the nitrate. It becomes warm when mixed with water, with formation of lanthanum hydroxide, $La(OH)_3$. The hydroxide reacts alkaline, absorbs carbon dioxide from the air, and is precipitated from solutions by caustic alkalies.

Lanthanum Chloride, $LaCl_3$, is a soluble salt which crystallizes with seven molecules of water.

Lanthanum Nitrate, $La(NO_3)_3 + 6H_2O$, is an easily soluble salt.

Lanthanum Sulphate, $La_2(SO_4)_3 + 9H_2O$, is much more soluble in cold than hot water.

Lanthanum Potassium Sulphate is precipitated when solutions of the two sulphates are mixed. It is completely insoluble in a solution of potassium sulphate.

Lanthanum Ammonium Sulphate, $La_2(NH_4)_2(SO_4)_4 + 8H_2O$, crystallizes in flattened striated prisms, soluble in water and permanent in air.

Erbium, Er.

Atomic Weight, 166.

This element occurs very sparingly associated with ytterbium and scandium. The metal is obtained as a gray powder from the chloride of erbium and sodium by electrolysis, and by reduction with sodium. It decomposes water with evolution of hydrogen.

Erbium Chloride, $ErCl_3$, is obtained by heating out of contact with air the residue from the evaporation of a solution of the oxide in hydrochloric acid, to which ammonium chloride has been added. It crystallizes from solution with six molecules of water.

Erbium Oxide, Er_2O_3, is a pale rose-colored powder obtained by ignition of the nitrate.

Erbium Nitrate, $Er(NO_3)_3 + 6H_2O$, separates in large crystals when a solution of the oxide in nitric acid is evaporated.

Erbium Sulphate, $Er_2(SO_4)_3$, crystallizes with eight molecules of water,

which are given off above 100°. The anhydrous salt is more readily soluble in water than the hydrous salt. With potassium sulphate it forms the double salt $K_2SO_4.Er_2(SO_4)_3 + 4H_2O$.

Ytterbium, Yb.

Atomic Weight, 173.

Ytterbium has not been obtained in the metallic state. It is a very rare element, found in only a few minerals. Euxenite thus far has been the best source of it.

Ytterbium Oxide, Yb_2O_3, is a white, heavy, infusible powder, which dissolves slowly in cold and easily in boiling dilute acids.

Ammonia precipitates from ytterbium solutions a hydroxide which absorbs carbon dioxide from the air. The hydroxide is easily soluble in acids, and on ignition leaves the oxide.

Ytterbium Nitrate changes on heating to a basic salt readily soluble in water.

Ytterbium Sulphate, $Yb_2(SO_4)_3$, is obtained by heating the nitrate with sulphuric acid until the excess of acid is expelled. A solution of the anhydrous salt in water yields on evaporation crystals of $Yb_2(SO_4)_3 + 8H_2O$, which are permanent in air.

Summary of the Third Group.

Boron, with the lowest atomic weight in the group, stands apart from the other members. It is non-metallic and acidic in character, and does not exhibit basic properties. Aluminum, with the next lowest atomic weight in the group, is both basic and acidic, showing the latter property in the aluminates. These compounds are analogous in composition to the ortho- and meta-borates. The ortho- and meta-aluminates are decomposed by carbon dioxide with separation of aluminum hydroxide, whereas the corresponding alkali borates are

converted by carbon dioxide into tetraborates. Gallium, indium, and thallium possess increasing basic properties in accord with their increasing atomic weights. Thallium, with the highest atomic weight, stands apart from the other members. The thallous halides resemble in insolubility the halides of silver and mercury, and thallous hydroxide is a strong base, which separates metallic hydroxides from salts.

The rare elements scandium, yttrium, lanthanum, erbium, and ytterbium are not as well understood as the other members of the group. The oxides of the group, thallium oxides and boric oxide excepted, are known as earthy oxides.

The student should tabulate the compounds of the group.

THE FOURTH GROUP.

THE members of this group are carbon, silicon, tin, and lead, and the rare elements titanium, germanium, zirconium, cerium, and thorium.

Carbon, C.

Atomic Weight, 12.

Carbon is a constituent of animal and plant matter, and of all organic compounds. It occurs in the air as carbon dioxide, and in the earth in rock masses of carbonates, and in the various forms of coal.

It exists in different allotropic modifications, which are classified as diamond, graphite, and amorphous carbon. Under the last are included gas carbon, anthracite coal, coke, charcoal, and lamp-black. These varieties differ in color, form, density, conductivity for heat and electricity, and in their behavior towards oxygen. The diamond, graphite, and gas carbon burn with difficulty, whilst charcoal and coke are easily combustible. All of the forms of carbon burn with oxygen to carbon dioxide. Charcoal is a poor conductor of electricity; graphite, coke, and gas carbon are good conductors, but the diamond does not conduct electricity. Graphite, and the denser forms of amorphous carbon, such as coke and anthracite, conduct heat better than charcoal. Carbon is infusible and non-volatile except in the electric arc, and is insoluble in all ordinary solvents, and resists the combined corrosive action of air and moisture.

The Diamond owes its value to its hardness and the brilliancy with which it reflects light. It is found crystallized in octahedral, dodecahedral, and more complex forms, often with curved edges. It varies in color from colorless, yellowish, green, red, blue to black. The density of pure specimens is 3.5, that of the black diamond is 3 or less. The diamond burns when heated intensely in air or oxygen to carbon dioxide, and leaves a small amount of incombustible ash.
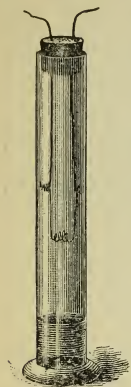
Exp. 191.—Enclose a small fragment of a diamond in a coil (Fig. 86) of small platinum wire connected with copper wire passing through a rubber stopper in the cylinder containing oxygen and some clear lime water. On heating the platinum with a battery current the diamond will take fire and burn brilliantly, and the lime water will react for carbon dioxide.

The diamond remains unchanged at a white heat out of contact with air, but at the intense heat of the electric arc it swells and changes to a coke-like mass.

As the diamond is the hardest of known substances, it can only be cut and polished by diamond dust. Only the transparent and more perfect stones are valuable as gems, which are cut so as to best reflect light. All the light which strikes the back planes at an angle greater than 24° 13′ is reflected. The weight of diamonds is commonly stated in carats, the carat being equal to 3.17 grains and 0.2054 gram.

Only the natural curved edges of diamonds answer for cutting glass. The cutting diamond simply makes a small crack in the glass, which determines the line of fracture. Writing diamonds are made of small splinters, which scratch but do not crack glass. Diamond dust is used in cutting and polishing precious stones. The black Brazilian diamonds have within a few years been employed in drilling rock, and consequently the price of them is much higher than formerly.

Graphite, also called plumbago and black-lead, occurs in foliated and in compact and granular masses, more rarely in hexagonal prisms. It is formed artificially in several ways. Molten cast iron dissolves more carbon than it can hold in combination on cooling, and the carbon partly separates as scales of graphite when the iron solidifies. Graphite is also produced when the concentrated black-ash liquors of soda manufacture are oxidized with nitre. Graphite has a brilliant metallic lustre, varying from an iron black to a steel gray. Its density is 2.5. It feels soft and greasy, and leaves a black mark when rubbed. Natural graphite contains earthy matters as impurities, and usually 0.5 to 1.3 per cent of hydrogen. It is purified by treatment with aqua regia and hydrofluoric acid, or with a mixture of sulphuric and nitric acids; also by heating with potassium chlorate and sulphuric acid. In the last process the residue is washed with water, and the product, which contains carbon, hydrogen, oxygen, and sulphuric acid, is dried and then heated, when it gives off gas and leaves pure graphite in the form of a fine powder. Graphite is less combustible than the diamond, and burns slowly and only at high temperatures in air and oxygen.

Exp. 192.—Cut the wood away from the lead of a pencil for two centimeters. Heat the end of the lead to redness in the lamp flame, and observe whether it burns or not.

The leads for leadpencils were formerly cut from blocks of compact graphite. In the improved process powdered graphite is mixed with fine clay, and the plastic mass is forced by great pressure through a hole, and thus formed into the shape required for pencils. Black-lead crucibles are made of a mixture of graphite and fire-clay. They are better conductors of heat, are more refractory, and less liable to crack than clay crucibles. They are much used in melting steel. Graphite is used as a lubricant and as a polishing powder, and also for facing sand moulds in iron foundries. It is the chief

ingredient of stove-blacking, and not only gives a good lustre but also prevents the iron from rusting. In the electrotype process the moulds are coated with powdered graphite, which serves as a conductor of electricity.

Gas Carbon collects on the upper part of the interior of the retorts in which coal is distilled in the manufacture of gas. The hydrocarbon vapors and gases are partially decomposed by the intense heat with separation of carbon. A similar result is obtained by passing ethylene gas, C_2H_4, one of the constituents of coal gas, through a white-hot porcelain tube. Part of the carbon deposits, and free hydrogen and complex hydrocarbons are formed. Gas carbon has a gray metallic lustre, and is very hard. Its density varies from 1.7 to 2.5. It is used for the carbon plates of the Bunsen battery, and for the carbon poles of the arc electric lamps.

Coke.—Certain varieties of bituminous coal when heated swell, become pasty, and after gases are no longer evolved, a porous mass remains, called coke. It is hard, has a grayish metallic lustre, and is a valuable fuel. It is formed in the retort in the manufacture of coal gas, and is made in enormous quantities by heating coal in suitable ovens. Coke contains besides carbon a little hydrogen, oxygen, and nitrogen, and the ash which was contained in the coal.

Lamp-black.—When a cold body is held in a luminous gas or lamp flame soot or lamp-black deposits. This is owing to the fact that the hydrogen burns first, leaving the carbon on the cold surface. Substances rich in carbon, such as kerosene oil, burn with smoky flames, and the amount of carbon separated may be increased by diminishing the supply of air. Lamp-black is manufactured by burning tar, rosin, turpentine, or petroleum with a small supply of air. The products of combustion pass through large chambers hung with coarse

sacking to collect the lamp-black. It is the basis of printing ink, and is used as a black pigment for various purposes. It contains hydrocarbons which may be partly expelled by ignition, but in order to remove the last traces of hydrogen it must be heated in chlorine, which combines with the hydrogen, but does not act upon the carbon.

Exp. 193.—Place a burning turpentine lamp under a bell-jar on a plate. Much lamp-black will separate.

Charcoal.—When pure sugar is heated in a platinum dish a porous glistening black residue remains, which contains a little oxygen and hydrogen even after intensely heating. By igniting this charcoal in pure chlorine pure carbon is obtained. It is tasteless, insoluble, conducts electricity, and has a density of 1.57. Sugar charcoal is useful in the laboratory when carbon free from ash is required.

Wood charcoal is made by covering a pile of wood with charcoal dust and moist earth. The wood is set on fire in suitable openings and allowed to burn slowly for some time ; then the openings are closed, and the pile is left until cold. A better yield of charcoal is obtained by subjecting wood to what is known as dry distillation in retorts or brick chambers, a process which admits of saving the liquid products of the distillation. Wood when dried at 150° contains about half its weight of carbon, the other half consisting of hydrogen and oxygen in nearly the proportion to form water, and a little nitrogen and ash. When the wood is charred, part of the carbon passes off with the volatile products, and the coal remaining differs in composition according to the temperature employed, as the following results of Violette's experiments with wood dried at 150° show :

Temperature.	Percentage yield of Charcoal.	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ash.
150°........	——	47.5	6.1	46 3	0.08
280°........	36.2	71.6	4.7	22.1	0.57
350°........	29.7	76.6	4.1	18.4	0.6
432°........	18.9	81.6	1.9	15.2	1.2
1032°........	18.7	81.9	2.3	14.1	1.6
1160°........	18.4	83.3	1.7	13.8	1.2
1300°........	17.5	90.8	1.6	6.5	1.1
1500°........	17.3	94.5	0.7	3.8	0.7
Over 1500°........	15.0	96.5	0.6	0.9	1.9

The table shows that charcoal made at low temperatures retains considerable hydrogen and oxygen, and that the amount of the product is diminished with increasing temperature of charring. Slow charring yields more charcoal than rapid, and dry wood more than wet. Heavy dense woods yield a denser and less porous coal than light soft woods. Charcoal made at 300° is brown and soft, and takes fire at about 380°; while that made at 1000°–1500° is black, hard, and brittle, and ignites at about 700°.

All solids possess the property of condensing gases on their surfaces at ordinary temperatures. Wood charcoal, owing to its porous structure, has an enormous extent of surface within its pores, and has the property in a marked degree of absorbing or condensing gases. The more porous the charcoal the greater the quantity of gas it will absorb. Hunter found that one volume of charcoal absorbed the following quantities of gases (reduced to 0° and 760 mm. pressure):

	Volumes.		Volumes.
Ammonia, ...	171.7	Carbon dioxide, . . .	67.7
Cyanogen, ...	107.5	Carbon monoxide, . .	21.2
Nitrous oxide, . . .	86.3	Oxygen, ...	17.9
Ethene, ...	74.4	Nitrogen, ...	15.2
Nitric oxide, . . .	70.5	Hydrogen, ...	4.4

The results show that the more readily condensible gases are absorbed in the greatest quantity. Gases contained in charcoal may be expelled by heat, and are mostly given off in a vacuum. Freshly ignited charcoal absorbs the gases of the atmosphere and aqueous vapor, and if the air is damp the charcoal takes up considerable water. The well-known property that charcoal possesses of removing noxious gases is due not only to their absorption within the pores, but to their oxidation to carbon dioxide and water by oxygen also absorbed. These products diffuse into the air almost as soon as formed, and the charcoal continues to absorb the noxious gas and oxygen, and bring about their combination. Thus it is that charcoal has the property of burning up the foul gases of the decay of bodies greater in weight than the charcoal used. It should be understood that charcoal, in the action just described, is not an antiseptic, but is simply a self-acting crematory, in which baneful products of decay are oxidized to the harmless products carbon dioxide and water. Charcoal retains this property for a long time, and when it has become impaired it can be restored by simply heating to redness.

Exp. 194.—Fill a tube over mercury with ammonia gas. Heat a cylindrical piece of charcoal to redness in a platinum crucible to expel the gases from it; then take the glowing coal with a pair of crucible tongs and put it into the glass tube without lifting the latter above the surface of the mercury. The gas will be rapidly absorbed, and the mercury will soon rise to the top of the tube. On removing the charcoal from the tube it will be evident from the odor that the ammonia which was absorbed is rapidly given off.

Exp. 195.—Place a small crucible filled with freshly ignited and nearly cold charcoal powder in a jar of hydrogen sulphide, then put it into a jar of oxygen. The rapid oxidation of the hydrogen sulphide will ignite the charcoal.

Exp. 196.—Hold a piece of charcoal under hot water in a test-tube by means of a glass tube or rod. Air will bubble from the charcoal, and if the latter is held under hot water long enough it will not float.

Exp. 197.—Place pieces of meat in three glass cylinders, and above the meat put a piece of wire gauze and a thin layer of cotton. Cover

the cotton in one cylinder with an inch of powdered charcoal. In the second cylinder place the same depth of dry fine earth, and in the third put dry sand. The meat will in a few days show marked indications of decay: that covered with sand will not have changed more than the others, but an odor will come from it; while no odor or a little ammonia will be noticed in the cylinders containing the charcoal and earth.

Animal Charcoal.—Wood charcoal has the property of withdrawing certain matters from solution and absorbing them in its pores. Animal charcoal possesses this power to a greater extent. It is made by calcining bones and other animal matter out of contact with air, and differs from wood charcoal in that it contains nitrogen. *Bone-black* is a black porous mass, consisting chiefly of calcium phosphate and carbon, obtained by heating bones. It is largely used in sugar-refining to remove coloring matter and lime salts from solutions of sugar. Bone-black is not adapted for decolorizing acid solutions which dissolve calcium phosphate, but blood charcoal is not open to this objection. It is made by evaporating and calcining a mixture of blood and potassium carbonate. The residue is exhausted with boiling water and hydrochloric acid, to remove the soluble portions, including the potassium salt which was added to make the product very porous. Animal charcoal is used in the laboratory to purify organic preparations, and in some cases to separate compounds from solutions. The following experiments illustrate some of the properties and uses of it:

Exp. 198.—Treat a highly diluted solution of acid quinine sulphate with bone-black. After a time the solution will not taste of quinine.

Exp. 199.—Decolorize with bone-black a very dilute solution of the coloring matter obtained by digesting logwood chips with water.

Mineral Coal is mainly of vegetable origin. The coal beds are the result of the slow decomposition under water and earth of plants, the change consisting of a loss of carbon dioxide, water, and marsh gas, and the formation of products

richer in carbon than the woody fibre of the plants. Coals are classified as non-flaming and flaming, according as they burn without or with a luminous flame. Anthracite, a non-flaming coal, burns with a pale-blue flame. It consists mainly of carbon, a little hydrogen, oxygen, nitrogen, and earthy matter or ash, and it yields from 4 to 7 per cent of volatile matter. The flaming coals contain more hydrogen and oxygen than anthracite. The varieties are: bituminous coal, which yields from 20 to 40 per cent of volatile matter; cannel or candle coal, so named because a small fragment burns readily like a candle, with 50 to 60 per cent of volatile ingredients; and brown coal, which is richer in oxygen than the other varieties. Peat, which is forming at the present time in bogs, more nearly approaches wood in composition.

The following are some analyses of coal and peat, and for the sake of comparison the composition of wood is also given:

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.
Wood, excluding ash, . .	50.00	6.00	44.00			
Peat, " " . .	59.70	5.70	33.04	1.56		
Brown Coal, Bovey, . . .	66.31	5.63	22.86	0.57	2 36	2.27
Cannel Coal, Wigan, . . .	80.07	5.53	8.10	2.12	1.50	2.70
Non-coking, Brial Hill, O. .	78.94	5.92	11.50	1.58	0.56	1.45
Non-coking, Indiana, . .	82.70	4.77	9.39	1.62	0.45	1.07
Coking Coal, Kentucky, .	74.45	4.93	13.08	1.03	0.91	5.00
Anthracite, Pennsylvania, .	90.45	2.43	2.45			4.67
" " .	92.59	2.63	1.61	0.92		2.25

Compounds of Carbon.

There are an enormous number of carbon compounds. With few exceptions they contain hydrogen and oxygen, and less frequently nitrogen. Many carbon compounds are formed by animal and plant growth, and from them many others are

prepared. Animals and plants develop from germs, and exhibit an *organized* structure: hence the carbon compounds derived from them have been termed *organic*. The study of the carbon compounds constitutes a branch of chemical science known as Organic Chemistry. Formerly compounds of carbon and hydrogen were only obtained from animal and vegetable substances; now a number of them can be formed synthetically, showing that there is no sharp distinction to be made between inorganic and organic compounds.

Carbon is tetravalent, and rarely exhibits a lower valence. Its oxides will be treated of first, then their derivatives; a few of the compounds of carbon and nitrogen will be described, and also a few of the simpler organic compounds.

Isomerism. —Compounds having the same composition and molecular weight, but differing in physical properties and chemical deportment, are said to be isomeric. The differences which isomers present are due to the different relations existing between the atoms in the molecule. While the *positions* of the atoms in a molecule are unknown, the *relations* of the atoms in many kinds of molecules are fixed with some degree of certainty, and are expressed by structural formulas. The existence of isomers renders some way of expressing their differences in constitution a necessity. For example, there are two isomeric compounds having the empirical formula C_2H_6O. One, methyl oxide, is a gas at common temperature, and the other is ethyl hydroxide or common alcohol. Their differences in chemical character are expressed by the formulas

$$\begin{array}{cc} \overset{\displaystyle H}{\underset{\displaystyle H}{H-C}}-O-\overset{\displaystyle H}{\underset{\displaystyle H}{C-H}}\ ; & \overset{\displaystyle H\ H}{\underset{\displaystyle H\ H}{H-C-C}}-O-H. \\ \text{Methyl oxide} & \text{Alcohol} \end{array}$$
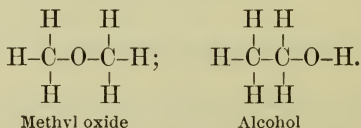
Polymerism. —Compounds having the same percentage composition but different molecular weights are said to be poly-

meric. For example, N_2O_4 is a polymer of NO_2, and benzene, C_6H_6, is a polymer of acetylene, C_2H_2.

Inorganic chemistry presents few examples of isomerism and polymerism: the best and most numerous examples are found among the compounds of carbon. Carbon appears to possess the property of forming complex and numerous compounds to a greater degree than other elements, and this property is in part explained by the theory that carbon atoms are linked to each other in such compounds.

Carbon Dioxide, Carbonic Anhydride, CO_2 or $O{=}C{=}O$, is a colorless gas with a slightly pungent odor and acid taste, and is commonly called carbonic acid. Carbon dioxide is formed when carbon or its compounds are burned in an excess of air or oxygen. Carbon in the form of charcoal burns with difficulty in oxygen freed from moisture by long contact with phosphorus pentoxide, but it burns with great brilliancy in oxygen containing traces of moisture. Hence it appears that water plays an important part in the ordinary burning of carbon. The nature of the action of the water is not understood.

In the formation of carbon dioxide 12 weights of carbon unite with 32 weights (2 volumes), of oxygen to form 44 weights and 2 volumes of carbon dioxide. The gas density of carbon dioxide is 22. These are the data for the molecular formula CO_2.

Exp. 200.—*a.* Suspend a small piece of charcoal on the platinum wire over the platinum spoon of the apparatus, Fig. 75, p. 155. Heat the charcoal intensely in a blast-lamp flame to expel volatile products, and allow to cool in a jar filled with carbon dioxide. Fill the apparatus with oxygen, then drop in some phosphorus pentoxide and adjust the stopper holding the spoon. Allow the apparatus to stand a day or longer in order to free the gas as completely as possible from moisture by long contact with phosphorus pentoxide. Heat by a battery current the platinum wire which supports the charcoal. The charcoal will burn slowly as long as the wire glows, and will cease to burn as soon as the wire cools.

b. Repeat the experiment with oxygen which has not been freed from water. The charcoal will burn brilliantly in the moist oxygen, and after the apparatus has cooled to the temperature of the room the volume of the gas will be the same as before the burning.

Carbon dioxide is made on a large scale in the manufacture of hydrogen sodium carbonate by burning anthracite or coke. It is commonly generated for laboratory and other uses, when it is required nearly pure, by treating marble (calcium carbonate) with dilute hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$
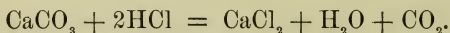
The gas thus prepared contains a trace of calcium chloride which is carried along with it mechanically, and also a little acid. By washing the gas with a solution of hydrogen sodium carbonate, and then passing it through a tube filled with cotton wool, these impurities may be almost completely removed. Pure carbon dioxide is best made by heating hydrogen sodium carbonate which decomposes as follows:

$$2HNaCO_3 = CO_2 + H_2O + Na_2CO_3.$$
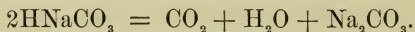
Carbon dioxide is 1.524 times heavier than air, and hence may be collected by displacing air. The critical temperature of carbon dioxide is 30°.9, below which point it condenses under pressure (at 0° under 36 atmospheres) to a colorless mobile liquid, boiling at −78°. When the liquid is exposed to the air a portion rapidly evaporates, and withdraws so much heat that the remainder is frozen to a white snow-like mass, which evaporates slowly. Solid carbon dioxide may be handled with impunity, as it is always surrounded by a gaseous layer which keeps it from actual contact with the skin. If, however, it is pressed between the fingers, it blisters the skin like a hot iron.

Carbon dioxide is one of the essential constituents of the atmosphere, which contains an average of 3 volumes of the

dioxide in 10,000 volumes. It is supplied to the atmosphere by the respiration of animals, by fires, and by the decay of animal and vegetable matter. The leaves of plants absorb it from the air, and in the presence of sunlight decompose it, setting free oxygen, and using the carbon to form vegetable matter. Thus the plants prevent the increase of carbon dioxide in the atmosphere.

Carbon dioxide has commonly been considered a poisonous gas, but its action is rather negative than positive. An increase in the amount of carbon dioxide in the air breathed is accompanied by a decrease in the amount of oxygen, thus producing oxygen starvation. Whenever the proportion of carbon dioxide in the air breathed reaches 10 per cent, the oxygen being correspondingly diminished, asphyxia results; and a diminution of the oxygen by one per cent may be followed by headache.

Carbon dioxide sometimes accumulates in wells and coal pits, where it is known as choke-damp. Its presence may be detected by lowering a burning candle, which will go out if the air is unsafe to breathe. A candle will not burn in air containing 4 per cent of carbon dioxide, but such air may be breathed for a short time.

Water dissolves its own volume of carbon dioxide gas at 15°, and at 0° 1.8 volumes. As the volume of a gas is inversely proportional to the pressure, so the quantity of the absorbed gas is proportional to the pressure. This is Dalton and Henry's law. According to this law, at double and triple the pressure water dissolves double and triple the amount of carbon dioxide.

Carbonated water, now so extensively used as a beverage, is made by dissolving carbon dioxide in water under pressure. The solution of the gas in water is facilitated by the addition of a little common salt, owing to the reaction between carbonic acid and sodium chloride, whereby hydrochloric acid and hydrogen sodium carbonate are formed, thus:

$$H_2CO_3 + NaCl = HCl + HNaCO_3.$$
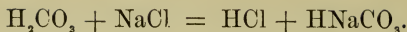
The effervescense of champagne, beer, soda-water, and other beverages is due to the escaping carbon dioxide.

Tests for Carbon and Carbon Dioxide.—Carbon dioxide reacts with a solution of calcium hydroxide to form an insoluble white precipitate of calcium carbonate :

$$O{=}C{=}O + Ca{<}^{OH}_{OH} = O{=}C{<}^O_O{>}Ca + H_2O.$$
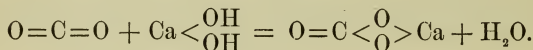
This reaction is applied in testing for free carbon dioxide. If it is in combination as in carbonates, the latter are treated with acids to set the gas free. All carbon compounds yield on burning in air, oxygen, or with oxidizing substances carbon dioxide, which may be detected in the products of the combustion by means of a solution of calcium hydroxide.

Exp. 201.—*a.* Burn charcoal in a jar of oxygen. Pour some lime water into the jar, and shake. The white precipitate which forms will dissolve with evolution of small bubbles of carbon dioxide on adding hydrochloric acid.

b. Burn charcoal, a splinter of wood, a bit of paper, and some coal gas in a jar filled with air, and test the products of each combustion for carbon dioxide.

Exp. 202.—Pour some clear lime water into a bottle fitted with tubes as in Fig. 87. Draw air into the lungs through the tube *A.* The air will bubble through the lime water, which will become slightly turbid owing to the carbon dioxide contained in the air. Next blow the air from the lungs slowly through *B*, and note the result.

FIG. 87.

Exp. 203.—Place in the generator (Fig. 52, p. 54) lumps of marble (calcium carbonate), pour in some water, and then add hydrochloric acid until the gas escapes freely. Add more acid from time to time as required.

Exp. 204.—*a.* Half fill a jar over water with carbon dioxide, then close the mouth of the jar with the hand and shake; open the jar under water. Repeat the shaking and opening under water as long as the gas is absorbed. Heat some of the carbonic acid water and note result, also test some of it by pouring it into lime water.

b. Expose a moist blue litmus paper to carbon dioxide gas collected over water. It will turn red, showing that moist carbon dioxide reacts acid. Dry the paper; the carbon dioxide will escape, and the test paper will turn blue. Also test carbonic acid water with litmus. In case the blue color is not restored on drying, the water probably contains hydrochloric acid carried over mechanically, and the experiment should be repeated with a fresh supply of water in the pneumatic trough.

Exp. 205.—Connect the delivery-tube of a siphon bottle of carbonic acid water by means of rubber tubing with an inverted cylinder filled with and standing over water. On allowing the water to escape from the siphon bottle gas will collect in the cylinder, which can be tested for carbon dioxide.

Exp. 206.—Into a jar filled with carbon dioxide thrust a burning splinter or taper. It will immediately be extinguished, as the gas does not support the combustion of carbon or compounds of carbon.

Exp. 207.—Ignite in a lamp flame a piece of magnesium ribbon, held by forceps, and place it in a pint or more of carbon dioxide. The metal will burn brilliantly in the gas, with formation of white magnesium oxide and separation of carbon in form of a black powder. The magnesium oxide may be removed by dissolving in hydrochloric acid. Other metals, notably potassium and sodium, decompose carbon dioxide and set free carbon.

Exp. 208.—*a.* Moisten the sides of a large glass jar with ammonia water, then pour in a little concentrated hydrochloric acid. A cloud of ammonium chloride will be formed. Pass into the jar a rapid stream of carbon dioxide. The cloud will indicate the upper surface of the gas. The gas in the jar may be poured into another vessel.

b. Fill a jar in which there is no cloud with the gas, by displacing air; then pour it into another jar, and test for the presence of the gas with a burning splinter. *c.* Dip a small jar into a large jar filled with the gas; then take out the small jar, and test the gas in it as before.

Carbonic Acid and Carbonates.

The two possible hydroxyl derivatives of tetravalent carbon are ortho-carbonic acid, $\begin{array}{c} HO \\ HO \end{array} > C < \begin{array}{c} OH \\ OH \end{array}$, and meta-carbonic

acid, $O = C <^{OH}_{OH}$. These have not been isolated, but their salts and ethers are well known. A solution of carbonic anhydride, CO_2, reacts acid to test paper, and doubtless contains carbonic acid—whether the ortho- or meta-acid has not been determined. Few ortho-carbonates of metals are known, but the meta-carbonates are numerous and important. There are two classes of the latter : the acid meta-carbonates, as hydrogen potassium carbonate, $O = C <^{OH}_{O-K,}$ and the normal meta-carbonates, as potassium carbonate, $O = C <^{O-K}_{O-K,}$ and calcium carbonate, $O = C <^{O}_{O} > Ca$.

Sodium Carbonate, Na_2CO_3 or $CO <^{O-Na}_{O-Na,}$ is manufactured on an enormous scale from common salt. Salt is converted into sodium sulphate by means of sulphuric acid. A mixture of sodium sulphate, coal, and calcium carbonate is heated in a flame oven. The coal reduces the sodium sulphate to sulphide, which at the same time reacts with the calcium carbonate to form sodium carbonate and calcium sulphide :

$$Na_2SO_4 + 4C \quad = Na_2S \quad + 4CO ;$$
$$Na_2S \quad + CaCO_3 = Na_2CO_3 + CaS.$$
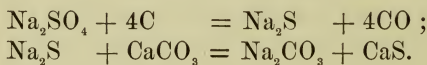
The fused mass of "black ash" thus obtained is treated with water, which takes up the sodium carbonate, leaving the calcium sulphide. The solution is evaporated, and the product is calcined in a flame oven to oxidize any sodium sulphide and to convert sodium hydroxide, which may have been formed by the action of lime, into carbonate. The crude sodium carbonate thus made constitutes the soda-ash of commerce.

Crystallized sodium carbonate, $Na_2CO_3 + 10H_2O$, known as "sal-soda," is obtained by allowing a solution of soda-ash

to crystallize at a winter temperature, when clear rhombic prisms form. Crystals of the decahydrated salt melt in their water of crystallization at 34°, with formation of the mono-hydrate, $Na_2CO_3 + H_2O$, which is also formed as a white powder when sal-soda is exposed to air.

Anhydrous sodium carbonate is obtained by drying crystals of sal-soda. It is a white powder which fuses at a red heat with slight loss of carbon dioxide. It is very soluble in water, and readily forms supersaturated solutions. Sodium carbonate reacts alkaline, and has the bitter taste of sodium hydroxide. It is extensively used in the manufacture of glass, sodium hydroxide, and hydrogen sodium carbonate.

Sodium carbonate occurs as an efflorescence on the soil of desert regions. It is the alkali of the plains of the western United States. It occurs in some lake waters in sufficient abundance for profitable extraction.

Exp. 209.—Dissolve 40 grams of soda-ash in 100 cc. of boiling water; filter, and leave the solution in a glass jar. In case crystals do not appear after the solution has stood a day or longer, drop in a fragment of a crystal of sal-soda to start the growth of crystals.

Exp. 210.—Determine the water of crystallization in sal-soda as follows. Weigh accurately a porcelain crucible; then put into it a clean uneffloresced piece of sal-soda (about 2 grams), and weigh again. Set aside for a week, and then weigh. Finally, heat the crucible and contents moderately with a lamp until after repeated weighing the weight remains constant. The crucible should not be placed upon the pan of the balance until cool to the touch. Calculate the per cent of water lost at ordinary temperature, and also the total loss after heating. Compare the results obtained with the per cent of $9H_2O$ and $10H_2O$ in $Na_2CO_3 + 10H_2O$.

Hydrogen Sodium Carbonate, $HNaCO_3$ or $CO {<} {OH \atop O-Na}$, is com-monly known as bicarbonate of soda or baking soda. It separates as a white powder when a strong solution of sodium carbonate is exposed for a time to carbon dioxide, the bicarbonate being less soluble than the carbonate. It is also formed

by the prolonged action of carbon dioxide on crystals of sal-soda :

$$CO <^{O-Na}_{O-Na} + 10H_2O + CO_2 = 2CO <^{OH}_{O-Na} + 9H_2O.$$
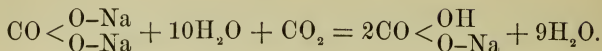
In the manufacture of bicarbonate of soda crystals of sal-soda are placed in shallow layers in chambers through which carbon dioxide is passed for a number of days. The carbon dioxide is obtained from the decomposition of magnesite, a native magnesium carbonate, or from limestone by acids, and also by the burning of coke and anthracite coal. The water liberated by the reaction flows off saturated with sodium carbonates, and the solution is evaporated to obtain the salt.

Hydrogen sodium carbonate has a feebly alkaline reaction, and a less acrid taste than sodium carbonate. A solution of hydrogen sodium carbonate gives off carbon dioxide on boiling, and the dry salt is resolved by heating into normal carbonate, carbon dioxide, and water.

$$2CO <^{OH}_{O-Na} = CO <^{O-Na}_{O-Na} + CO_2 + H_2O.$$
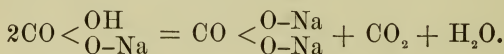
Few salts are so commonly used as bicarbonate of soda.
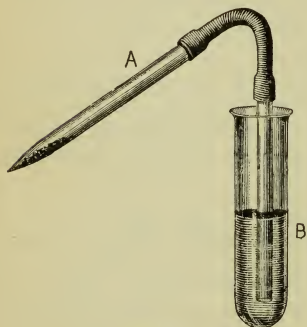
FIG. 88.

Baking-powders are mixtures of it with hydrogen potassium tartrate (cream of tartar), or some other salt. Baking-powder remains unchanged when dry, but on dissolving in water gives off carbon dioxide gas. When a mixture of flour and baking-powder and water is made, the gas set free inflates or raises the dough. One gram of hydrogen sodium carbonate yields, when decomposed by an acid, about 260 cc. of gas. Bicarbonate

of soda is used in medicine as a mild anti-acid. With tartaric acid, and also with cream of tartar, it constitutes effervescing aperient powders.

Exp. 211.—Place in the A, Fig. 88, some hydrogen sodium carbonate; heat, and allow the gas evolved to pass into lime water in the test-tube B. Note observations.

Exp. 212.—Mix 15 grams of hydrogen potassium tartrate with the weight of hydrogen sodium carbonate required by the equation

$$HKC_4H_4O_6 + HNaCO_3 = NaKC_4H_4O_6 + CO_2 + H_2O.$$

Hydrogen potassium   Sodium potassium
tartrate   tartrate
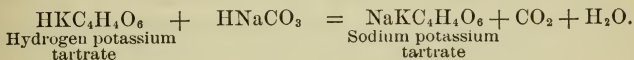
Observe whether any change occurs when the two salts are mixed, then place the mixture in a flask and pour in 100 cc. of water. Note the result. Heat to boiling, and filter the solution into a porcelain dish, and let stand for several days. Large crystals of sodium potassium tartrate (Rochelle salt) will form.

Potassium Carbonate, K_2CO_3 or $CO{<}{{O-K}\atop{O-K}}$, is the chief ingredient of potash obtained by leaching wood ashes with water and evaporating the solution to dryness. The product is called potash, or potashes, because the lye from the ashes was formerly, and is in some localities at the present time, boiled down in iron pots. The impurities in crude potash are potassium chloride, sulphate, and silicate, sodium salts, and other substances. In order to purify potash it is treated with a small quantity of hot water, which takes up the potassium carbonate and leaves most of the impurities undissolved. The solution is evaporated, and the residue is heated to redness. The purified product, from its pearly appearance, is known as pearl ash. Formerly wood ashes were the only source of potash, but in recent years large quantities have been obtained from beet-root molasses, wool washings, and potassium sulphate.

Pure potassium carbonate is best prepared by igniting hy-

drogen potassium carbonate, a salt which can be easily obtained pure.

Potassium carbonate is a white solid, which deliquesces in moist air to an oily liquid, and dissolves in less than its weight of water at ordinary temperature. It has a strong alkaline reaction and taste. It is used in the manufacture of other potassium salts, glass, and soft soap.

Exp. 213.—Place half a pint to a pint of wood ashes upon a filter, and pour on an equal bulk of boiling water. After the water has mostly filtered through, pour it back again upon the ashes. Evaporate the solution obtained to dryness. Place a small portion of the residue in a test-tube, and add to it hydrochloric acid. An effervescence may be regarded as proof of the presence of a carbonate. To the remainder of the residue add a little water. A portion will remain undissolved. Test the reaction of the solution.

Hydrogen Potassium Carbonate, $HKCO_3$ or $CO < \begin{smallmatrix} OH \\ O-K \end{smallmatrix}$, is commonly known as bicarbonate of potash, from the old formula $K_2O.2CO_2.H_2O$, carbonate of potash being in the same system $K_2O.CO_2$. It has also been called saleratus (aerated salt), since it is obtained by the action of an aeriform body upon a salt. It is prepared by passing carbon dioxide gas through a concentrated solution of potassium carbonate, when the less soluble hydrogen potassium carbonate will separate in crystals. It has a slightly alkaline reaction and saline taste. It dissolves in about 4 parts of water at ordinary temperature. The solution loses carbon dioxide when boiled, and the dry salt is completely decomposed by heat into potassium carbonate, carbon dioxide, and water. Bicarbonate of potash was formerly used in cookery, but has been replaced by the cheaper bicarbonate of soda.

Commercial Ammonium Carbonate is manufactured by subliming a mixture of chalk (calcium carbonate) and ammonium sulphate or chloride. It is a compound of equal molecules of

hydrogen ammonium carbonate and ammonium carbamate, $HNH_4CO_3 + NH_2NH_4CO_2$. It is a colorless translucent fibrous mass, which on exposure to the air falls to a white powder of hydrogen ammonium carbonate, the carbamate slowly decomposing and giving off ammonia. The commercial salt has a strong ammoniacal odor, and on this account is used in "smelling salts." It is used in medicine, and in the laboratory for precipitating carbonates.

Ammonium Carbonate, $(NH_4)_2CO_3 + H_2O$ or $CO<^{O-NH_4}_{O-NH_4} +$ H_2O, is obtained as a crystalline powder when the commercial carbonate is digested for a time at 12° with aqueous ammonia. From a solution saturated at 30° to 35° it separates in transparent crystals. These lose ammonia, and change to the hydrogen ammonium carbonate.

Hydrogen Ammonium Carbonate, HNH_4CO_3 or $CO<^{OH}_{O-NH_4}$, is obtained when a concentrated solution of the commercial carbonate is saturated with carbon dioxide. It forms crystals which do not smell of ammonia nor lose their lustre in dry air. It is completely decomposed on warming into ammonia, carbon dioxide, and water.

Calcium Carbonate, $CaCO_3$ or $CO<^O_O>Ca$, is the most abundant calcium compound in nature. It is dimorphous, occurring as calcite, crystallized in the hexagonal system, and having a density of 2.7, and as arragonite in the rhombic system, density 2.9. Limestone, marble, the shells of mollusca, egg-shells, coral, and chalk are chiefly calcium carbonate. It may be made by mixing solutions of an alkali carbonate and a calcium salt. If the precipitation is made at ordinary temperature the fine white powder which separates consists of the calcite form of crystals. But if the precipitation is made boiling hot the crystals are larger, and have the arragonite form.

Calcium carbonate is slightly soluble in pure water, 1 liter of cold or boiling water dissolving about 18 milligrams. It is more soluble in water containing carbonic acid. One liter of water saturated with carbonic acid dissolves at 10° 0.88 gram of calcium carbonate. Calcium carbonate separates on boiling, but the solution still contains 34 milligrams of it per liter.

The carbonic acid solution of calcium carbonate loses carbon dioxide on exposure to air, and calcium carbonate precipitates. The natural waters of limestone regions contain calcium carbonate, and the stalactites and stalagmites of caves are formed by the gradual deposition of it. The "hardness" of natural waters is chiefly due to calcium carbonate.

Exp. 214.—To a dilute solution of calcium chloride add a solution of sodium carbonate so long as a precipitate forms. Heat to boiling, then collect the precipitate on a filter, and wash moderately. Test a portion of the precipitate for carbon dioxide. Represent by an equation the reaction between the calcium chloride and sodium carbonate.

Exp. 215.—*a.* Dilute lime water with its bulk of water, and pass carbon dioxide through it until a clear solution results. *b.* Leave a portion of the solution in an open bottle, to find whether a precipitate forms after some days. *c.* Boil another portion until calcium carbonate separates. *d.* To some of the solution add a solution of soap, and observe the formation of an insoluble lime soap.

Strontium Carbonate, $SrCO_3$ or $CO<^O_O>Sr$, occurs as strontianite, density 3.6 to 3.7. It is prepared from soluble strontium salts by the method described for the preparation of calcium carbonate.

Barium Carbonate, $BaCO_3$ or $CO<^O_O>Ba$, occurs as witherite, density 4.3. It is best prepared pure by precipitating a solution of barium chloride with ammonium carbonate. It is used in chemical analysis and for the preparation of barium salts.

The carbonates of the alkali-earth metals present a gradation of properties with the increasing atomic weights of the metals. Strontium carbonate is more soluble in water than calcium carbonate, and barium carbonate is more soluble than strontium carbonate. Calcium carbonate is converted into oxide at a red heat, and barium carbonate fuses and decomposes only at very high temperatures. Strontium carbonate is intermediate in these properties between calcium carbonate and barium carbonate.

Magnesium Carbonate, $MgCO_3$ or $CO<^O_O>Mg$, occurs as magnesite. This mineral does not lose carbon dioxide at 300°, and is but slightly acted upon by cold acids. Magnesium carbonate cannot be prepared by precipitating a solution of a magnesium salt with an alkali carbonate, as the precipitate has the composition described under magnesia alba. It has been obtained with 3 and 5 molecules of water by allowing a solution of hydrogen magnesium carbonate to stand in a partially closed flask.

Hydrogen Magnesium Carbonate, $Mg(HCO_3)_2$ or **HO–CO–O–Mg–O–CO–OH,** is not known in the solid state, but is probably formed when magnesia alba dissolves in water containing carbon dioxide. Engel and Ville found that one liter of water containing carbon dioxide will dissolve at

1 atmosphere and 19°.5, ...	25.79 grams of $MgCO_3$.
7.5 atmospheres and 19°.5, . . .	51.2 " " "
765 mm. and 70°, ...	8.1 " " "
765 " " 100°, ...	0 " " "

The solutions contained very nearly one atom of magnesium to two molecules of carbon dioxide, the proportion required by the formula $Mg(HCO_3)_2$.

Magnesia Alba is a varying mixture of magnesium carbonate

and hydroxide. It is made by adding sodium carbonate to a solution of a magnesium salt. The precipitate is washed with water and dried. It is also made by decomposing a solution of the hydrogen magnesium carbonate with a current of steam. Magnesia alba is almost insoluble in water, but dissolves readily in acids. It is used in medicine, and in the preparation of other magnesium compounds.

Carbon Monoxide or Carbonic Oxide, CO, is formed when carbon dioxide is in contact with glowing carbon, as charcoal and coal :

$$\underset{\text{2 vols.}}{CO_2} + C = \underset{\text{4 vols.}}{2CO}.$$
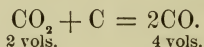
Hence it is produced when carbon burns in an insufficient supply of air.

Exp. 216.—*a.* Heat to redness in a gas combustion furnace or a coal fire fragments of charcoal contained in a piece of iron gas-pipe three quarters of an inch in diameter. The pipe may be conveniently bent in the form of a U tube if it is to be heated in a stove. Pass a slow stream of carbon dioxide into one end of the pipe. The gas which issues from the other end of the hot pipe will burn with the characteristic blue flame of carbonic oxide. *b.* Pass oxygen into the tube. Carbonic oxide will be obtained as before.

The experiment illustrates the changes which take place in an anthracite fire. The oxygen of the air entering at the grate bars combines with the carbon to form carbon dioxide, which passes upward through the glowing coals and is changed to carbonic oxide. If air is supplied over the coal the carbonic oxide burns with a characteristic blue flame, providing the temperature is sufficient for its ignition. When carbon burns only to the monoxide less than one third as much heat is obtained as when it burns to the dioxide ; thus, 12 grams of carbon in uniting with 16 grams of oxygen to form CO

evolve 28,800 calories, while the same weight of carbon combining with 32 grams of oxygen to form CO_2 will evolve 96,800 calories.

Carbonic oxide may be obtained pure in a number of ways. A good method is to heat oxalic acid and oil of vitriol together in a flask. The heat and oil of vitriol remove water from the oxalic acid, and liberate equal volumes of carbonic oxide and carbon dioxide :

$$\begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} = H_2O + CO + CO_2.$$
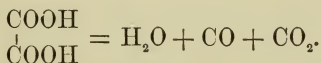
The carbon dioxide is then absorbed by a solution of sodium hydroxide or by milk of lime.

Carbonic oxide is a colorless tasteless gas, with a peculiar feeble odor. It has a density of 14, which is little less than that of air. It is but slightly soluble in water. It condenses under a pressure of one atmosphere at $-190°$ to a colorless transparent liquid which solidifies in vacuum at $-211°$.

Carbonic oxide is very poisonous, small quantities in the air inhaled causing headache and insensibility. It unites with the coloring matter of the blood, forming a definite compound, which can be detected by means of the spectroscope. The characteristic spectrum of this compound reveals the cause of death in cases of poisoning with illuminating gas.

Carbon monoxide burns in air or oxygen with formation of carbon dioxide.

Exp. 217.—Fill a jar over water with carbon monoxide, and pour into the jar some lime water. If the gas is free from carbon dioxide the lime water will remain clear. Set fire to the gas, and when it has ceased burning close the jar with the hand and shake. A white precipitate is evidence of the formation of carbon dioxide.

It has been found that a mixture of perfectly dry carbonic oxide and oxygen is not ignited by a glowing platinum wire nor by the electric spark, and the following experiment shows

that a flame of carbonic oxide is extinguished when thrust
into dry air.
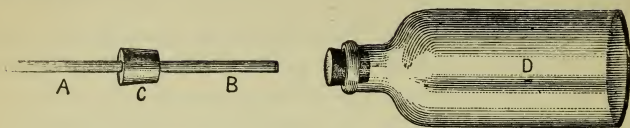
Exp. 218.—The bottle *D*, Fig. 89, has a capacity of a litre or more.
In order to dry the air in it, pour some concentrated sulphuric acid into
the bottle, and allow it to remain corked some minutes. Pass carbonic
oxide through a tube filled with fragments of potassium hydroxide, to
free the gas from moisture, and then through the tube *AB*. Ignite the
gas at *B*, remove the cork from *D*, and thrust the flame into *D*, placing
the stopper *C* in the neck of the bottle. The flame will be extinguished
if the air in the bottle is dry. Repeat the experiment, using a bottle with-
out attempting to dry the air.

Traube explains the action of water in the burning of car-
bonic oxide by the following equations :

$$(1) \quad CO + 2H_2O + O_2 = CO(OH)_2 + H_2O_2.$$
$$(2) \quad H_2O_2 + CO \quad\quad = CO(OH)_2.$$
$$(3) \quad 2CO(OH)_2 \quad\quad = 2CO_2 + 2H_2O.$$
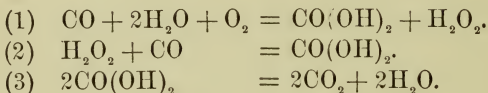
Equation 1 represents the formation of carbonic acid and hy-
drogen dioxide. In support of this view is the fact that
hydrogen dioxide is obtained when carbonic oxide is burned
from a jet on the surface of water.

At a red heat carbonic oxide reduces many metallic oxides,
and plays an important part in many metallurgical processes.

Exp. 219.—Place some cupric oxide in a hard glass tube, and heat the
part of the tube about the oxide. Pass into the tube carbonic oxide,
and pass the gaseous product of the combustion into lime water. Note
observations, and write the equation representing the reaction between
the cupric oxide and carbonic oxide.

Carbonyl Chloride, $CO<^{Cl}_{Cl}$.—This compound is formed when a mixture of equal volumes of dry chlorine and carbon monoxide is exposed to light. Carbonyl chloride at ordinary temperature is a suffocating gas. It is decomposed by water, with formation of carbon dioxide and hydrochloric acid :

$$COCl_2 + H_2O = 2HCl + CO_2.$$
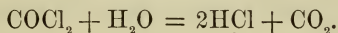
The radical CO in combination is termed carbonyl.

Carbon Disulphide, CS_2, is formed by the direct union of sulphur vapor with glowing charcoal. When charcoal is heated to the temperature of ignition in oxygen it continues to burn with evolution of sufficient heat to maintain it above the temperature of ignition. In the union of carbon and sulphur, on the contrary, heat is absorbed, and hence it is necessary to keep up the temperature by external heating. 12 grams of carbon unite with 64 grams of sulphur with a thermal result of $-$ 12,600 calories.

Carbon disulphide is a colorless, mobile liquid, which refracts light strongly, boils at 46°, and has an odor something like that of chloroform. Its vapor ignites at 149°, burning with a blue flame, with formation of carbon dioxide and sulphur dioxide. Large quantities of it are used to destroy vermin, as its vapor is poisonous. It is used in the arts as a solvent for caoutchouc, fats, and other substances.

The commercial carbon disulphide has often a very disagreeable odor, due to impurities. It may be purified by distilling it from a flask filled with lumps of quick-lime.

Thiocarbonic Acid, H_2CS_3.—Carbon disulphide reacts with a solution of sodium sulphide to form sodium thiocarbonate, thus:

$$CS_2 + Na_2S = Na_2CS_3.$$
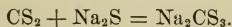
Hydrochloric acid decomposes the thiocarbonate with separation of thiocarbonic acid, a yellow oil of disagreeable odor, which readily de-

composes into hydrogen sulphide and carbon disulphide. A number of salts of the acid are known, but they are of little importance. It should be noticed that H_2CS_3 is the analogue of H_2CO_3, which has not been isolated.

Carbonyl Sulphide, COS, is formed when sulphur vapor and carbonic oxide are passed together through a hot tube. It is best obtained by other methods. It is a colorless gas, somewhat soluble in water, to which it imparts its peculiar odor and taste. It is supposed to exist in some sulphur waters.

Carbamic Acid, $CO{<}^{OH}_{NH_2}$.—When dry ammonia gas and carbon dioxide are mixed the two unite to form the ammonium salt of carbamic acid having the formula $CO{<}^{ONH_4}_{NH_2}$. The salt can be easily obtained in crystals by passing the dry gases into well-cooled absolute alcohol. Free carbamic acid is unknown.

Carbamide or Urea, $CO{<}^{NH_2}_{NH_2}$.—This compound, like the preceding, is an amide[*] of carbonic acid. It is derived from the chloride of carbonic acid by the action of ammonia:

$$CO{<}^{Cl}_{Cl} + 2NH_3 = CO{<}^{NH_2}_{NH_2} + 2HCl.$$
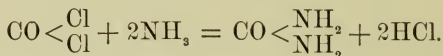
Urea exists to the amount of 2 or 3 per cent in human urine, from which it was originally obtained. In 1828 Wöhler discovered that it can be formed by heating an aqueous solution of ammonium cyanate, whose atoms rearrange themselves to form urea:

$$O = C = N\text{–}NH_4 = O{=}C{<}^{NH_2}_{NH_2}.$$
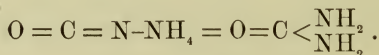
This was an important discovery, as it was the first instance

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[*] For the general character of amides, see Compound Ammonias, p. 352.

of the preparation of an organic compound from inorganic substances.

Cyanogen Compounds.

The univalent radical cyanogen, CN, exists in a large number of compounds. Cyanogen is an acid-forming radical, somewhat similar in properties to the atom of chlorine. It was first obtained by Gay-Lussac in 1815, who, in his investigations of its compounds, was the first to show that a group of elements can act chemically as a simple element. It is one of the best examples known of a compound radical. Carbon and nitrogen do not unite directly, unless perhaps under the influence of the induction spark. All nitrogenous organic compounds on ignition with metallic sodium yield sodium cyanide, and animal matter when heated with potassium carbonate yields potassium cyanide. Free nitrogen is absorbed by a glowing mixture of charcoal and potassium carbonate, with formation also of potassium cyanide.

Cyanogen Gas, $\Big\}$ C_2N_2 or $\begin{matrix} C\equiv N \\ | \\ C\equiv N \end{matrix}$.—This compound is a color-
Dicyanogen,

less, highly poisonous gas, with a peculiar odor resembling that of peach kernels. It has a density of 26, corresponding to the formula C_2N_2. It condenses at low temperatures, or under pressure to a liquid which boils at $-20°.7$ and freezes to a crystalline mass melting at $-34°$. Cyanogen gas is best prepared by heating mercuric cyanide :

$$Hg{<}^{CN}_{CN} = Hg + \begin{matrix} CN \\ | \\ CN \end{matrix}.$$
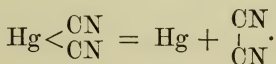
The gas must be collected over mercury, as it is soluble in water and alcohol. It burns with a characteristic purple

flame, with formation of carbon dioxide, nitrogen being set free. The aqueous solution of cyanogen soon undergoes change, with formation of hydrocyanic acid, oxalic acid, ammonia, carbon dioxide and urea, and deposition of a brown substance known as azulmic acid. Acids retard the decomposition.

Exp. 220.—Heat dry mercuric cyanide in a hard glass tube and burn the escaping gas. The brownish-black residue remaining is paracyanogen.

Paracyanogen, $(CN)_x$.—This substance is obtained as described in the foregoing experiment. It has the same proportions of carbon and nitrogen as cyanogen, into which it is converted at 840°. Its molecular weight is unknown.

Hydrocyanic Acid, HCN or H–C≡N, is formed by the action of acids on cyanides. It is best obtained by pouring a cold mixture of 7 parts of oil of vitriol and 14 parts of water upon 10 parts of coarsely powdered potassium ferrocyanide contained in a large retort. The neck of the retort is inclined upwards, so that only the more volatile portions will pass over during the distillation. In order to free the vapor from water it is passed through U tubes containing calcium chloride heated to 30°. The dry gas is condensed in a well-cooled receiver. In the preparation of an aqueous solution the vapors are cooled and received in water.

Pure anhydrous hydrocyanic acid boils at 26°.5. It is soluble in all proportions in water, alcohol, and ether. It has the odor of bitter almonds. Its aqueous solution is known as *prussic acid*. This decomposes on keeping into formic acid, ammonia, and other bodies. Traces of mineral acids retard this decomposition. Hydrocyanic acid is very poisonous, and very rapid in its action. The vapor when inhaled causes almost instant death, and in small quantities produces headache and other troubles. An internal dose of $\frac{1}{20}$ of a grain is

usually fatal to the human subject. The antidotes recommended are chlorine water and ammonia.

Potassium Cyanide, KCN.—The pure salt is prepared by passing the vapor of hydrocyanic acid into an alcoholic solution of potassium hydroxide when the salt separates in small crystals. Commercial potassium cyanide is made by melting dry potassium ferrocyanide. Potassium carbonate mixed with the ferrocyanide increases the yield, but the product is not as pure.

Potassium cyanide is a white crystalline solid, very soluble in water. It is decomposed by acids, with evolution of hydrocyanic acid. The salt smells of this acid, which is set free by the carbonic acid of the air. Hence potassium cyanide is kept in well-stoppered vessels. It is used in large quantities in electro-plating and in photography, and is a valuable reagent in the laboratory. It is exceedingly poisonous.

Silver Cyanide, AgCN, is similar in properties to the chloride, bromide, and iodide of silver. It separates as a white precipitate when a solution of hydrocyanic acid is added to silver nitrate. It is insoluble in nitric acid, but easily soluble in ammonia, and is not changed by light. It dissolves readily in potassium cyanide, and the solution on evaporation yields crystals of the double salt $KAg(CN)_2$, which are soluble in four parts of water and are permanent in air. Mention has already been made of the use of this compound in electro-plating.

Cyanides of Copper.—Potassium cyanide produces in a cold solution of copper sulphate a yellowish precipitate of cupric cyanide, $Cu(CN)_2$, which soon loses cyanogen and changes into $Cu_2(CN)_2.Cu(CN)_2$. This on heating changes to cuprous cyanide, which is white. The cyanides of copper are insoluble in water, but dissolve readily in potassium cyanide. Such solutions are used in electro-plating with copper.

Trihydrocyanic Acid, $H_3C_3N_3$.—This compound is formed when an aqueous solution of hydrocyanic acid, to which a few drops of potassium hydroxide have been added, is allowed to stand. It fuses at 180°, and at higher temperatures is resolved into hydrocyanic acid gas.

Cyanogen Chloride, $CNCl$, and Cyanuric Chloride, $C_3N_3Cl_3$, possess gas densities corresponding to their formulas.

Normal Cyanic Acid, $N\equiv C-OH$, is unknown in the free state, but there are ethers of it, as for example methyl cyanate, $N\equiv C-O-CH_3$.

Isocyanic Acid, $O=C=N-H$, is also called carbimide.* It is best prepared by heating cyanuric acid:

$$C_3N_3(OH)_3 = 3OCNH.$$
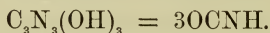
The vapors are passed into a vessel surrounded by a freezing mixture. On removing the liquid obtained from the freezing mixture it becomes hot, and changes to a porcelain-like mass of cyamelide, a compound of unknown molecular weight.

Potassium Isocyanate, $O=C=N-K$, is formed when potassium cyanide is melted in air, or better with some oxide such as manganese dioxide or red lead. Cyanates do not yield cyanic acid when treated with an acid, but are decomposed with evolution of carbon dioxide and formation of an ammonium salt, thus:

$$O=C=N-K + 2HCl + H_2O = KCl + NH_4Cl + CO_2.$$

Exp. 221.—Fuse in a glass tube or an iron spoon a little potassium cyanide to which some red lead has been added. When the mass has

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* An imide is a compound derived from ammonia by the replacement of two atoms of hydrogen by a bivalent acid radical, and hence contains the group NH.

cooled dissolve some of it in water, and under a hood with a good draught add hydrochloric acid to acid reaction, and heat the solution to boiling. Add an excess of potassium hydroxide to the acid solution and boil again; ammonia will escape freely. Impure potassium cyanide containing a little cyanate with similar treatment gives a little ammonia, but not as much as obtained from the cyanate.

Cyanuric Acid, $C_3N_3(OH)_3$, crystallizes from an aqueous solution with two molecules of water. It results from the action of water on cyanuric chloride:

$$C_3N_3Cl_3 + 3HOH = C_3N_3(OH)_3 + 3HCl.$$
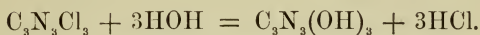
It is best obtained by passing chlorine over melted urea when the following reaction takes place:

$$3CO(NH_2)_2 + 3Cl = N + HCl + 2NH_4Cl + C_3N_3(OH)_3.$$

Thiocyanic or Sulphocyanic Acid, $N\equiv C-S-H$, is a colorless liquid with an odor similar to that of strong acetic acid. It is obtained anhydrous when dry hydrogen sulphide is passed over the mercuric salt. Thiocyanates are formed by the direct union of sulphur with a cyanide, as when potassium cyanide and sulphur are fused together. The ammonium salt is formed when prussic acid is warmed with yellow ammonium sulphide:

$$(NH_4)_2S_2 + HCN = NH_4SH + NCSNH_4.$$
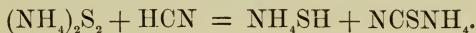
Ammonium thiocyanate is best prepared as follows. A mixture of 8 parts of carbon disulphide, 30 parts of alcohol, and 30 parts of concentrated ammonia is allowed to stand until the carbon disulphide is dissolved, when the solution is concentrated. It yields on cooling crystals of the salt. The changes which occur in this process are complicated. The ammonia and carbon disulphide react to form intermediate products, which are decomposed, when the solution is heated, with formation of ammonium thiocyanate.

Ammonium or potassium thiocyanate is used in testing for ferric salts, to whose solutions it imparts a red color, ferrous salts giving no coloration with the reagent.

Methane and Derivatives.

Methane or Marsh Gas, CH_4. Gas density, 8.—Methane is the simplest compound of carbon and hydrogen known, and is, next to hydrogen, the lightest known gas. It is formed in marshes by the slow decomposition of vegetable matter under water. It is the "fire-damp" of coal mines, and is contained in the mixture of gases from natural-gas wells. It may be obtained synthetically by passing a mixture of carbon disulphide and hydrogen sulphide over glowing copper:

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$
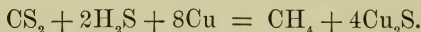
Hence methane may be formed from substances which are not products of animal or plant growth. Methane is commonly prepared by heating a mixture of sodium acetate and sodium hydroxide:

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3.$$

Exp. 222.—Heat an intimate mixture of 1 part of sodium acetate and 4 parts of soda-lime (a mixture of sodium hydroxide and lime) in a hard glass tube or other suitable vessel. Collect the gas over water. Lift a jar of the gas from the water, and before turning the mouth of the jar upwards ignite the gas. Mix 1 volume of the gas with 10 volumes of air and ignite. Mix 1 volume of the gas with 2 volumes of oxygen in a stout tube of 50 cc. capacity. Wrap the tube in a towel for safety, and ignite the gas.

Methane made from sodium acetate contains a few per cent of hydrogen and a little ethylene, C_2H_4. The latter may be removed by passing the gas through a tube filled with pumice stone drenched with strong

sulphuric acid. The presence of ethylene increases the luminosity of burning methane. Methane from sodium acetate after remaining in a gas-holder several days is sufficiently pure for experiments. The water in the gas-holder slowly absorbs the impurities, which add to the light of the burning gas.

Methane is colorless and odorless, and but slightly soluble in water. Mixed with sufficient air or oxygen, it burns with explosive violence, with formation of carbon dioxide and water.

The four hydrogen atoms of methane may be successively replaced by chlorine aided by sunlight, with formation of chlorine substitution products of methane, thus:

$$
\begin{aligned}
CH_4 &+ Cl_2 = CH_3Cl + HCl; \\
CH_3Cl &+ Cl_2 = CH_2Cl_2 + HCl; \\
CH_2Cl_2 &+ Cl_2 = CHCl_3 + HCl; \\
CHCl_3 &+ Cl_2 = CCl_4 + HCl.
\end{aligned}
$$
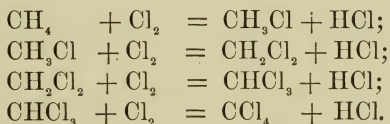
The reactions are of theoretical interest, but in practice the substances are obtained by other methods.

The group remaining after the replacement of part of the atoms of a molecule is frequently called a "residue" or a "rest:" the latter is the German term. Such a group is obviously a compound radical. For example, by substituting an atom of chlorine for one of hydrogen in CH_4 we have CH_3Cl, and CH_3 is a residue or radical. It is called methyl, and CH_3Cl methyl chloride.

To indicate the derivation of methyl chloride from methane it is also called monochlormethane. The other chlorine substitution products for the same reason are termed di-, tri-, and tetra-chlormethane.

Methyl Chloride, CH_3Cl, is now obtained in large quantities as a by-product in the manufacture of beet sugar. It boils at $-23°$. The pressure of its vapor at ordinary temperature is only 4 or 5 atmospheres. Methyl chloride is used for producing

low temperatures by evaporation, and in the manufacture of aniline dyes.

Methyl Iodide, CH_3I, is a colorless liquid boiling at 44°. It has an ethereal odor, and partially decomposes in light with separation of iodine. It is prepared by adding iodine gradually to methyl alcohol and phosphorus:

$$10CH_3OH + 10I + 2P = 10CH_3I + 2PO(OH)_3 + 2H_2O.$$

Chloroform or Trichlormethane, $CHCl_3$, is obtained by distilling a mixture of chloride of lime, common alcohol, and water. It has an agreeable odor, and a sweetish, burning taste. It boils at 61°, is almost insoluble in water, but mixes in all proportions with alcohol, ether, and other organic liquids. It is a solvent for bromine, iodine, phosphorus, and many organic compounds. The vapor of chloroform when inhaled produces insensibility; hence its use in surgery.

Methyl Alcohol, CH_3OH, is one of the products of the destructive distillation of wood. The wood alcohol or wood spirit of commerce is a mixture of methyl alcohol, acetone (C_3H_6O), water, and other compounds. It is used in place of common alcohol as a solvent and for burning, and is used in the preparation of methyl compounds. Its vapor when inhaled for some time causes headache. In England it is mixed with common alcohol to render the latter unfit for use in the manufacture of beverages. The object of this is to avoid the tax which is placed on common alcohol.

Pure methyl alcohol is obtained by the decomposition of certain methyl compounds. It boils at 55°.1, mixes in all proportions with water, and burns with a pale-blue flame. It is similar to common alcohol in chemical properties.

Formaldehyde, $HCHO$, is the first of a series of compounds known as aldehydes which are formed from alcohols by the

removal of two atoms of hydrogen by partial oxidation. Methyl alcohol is converted into aldehyde by the following reaction:

$$CH_3OH + O = HCHO + H_2O.$$
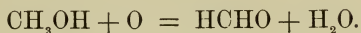
Formaldehyde is an unstable compound, uniting with oxygen to form formic acid.

Formic Acid, HCOOH, is so called because it was first obtained by distilling red ants (*Formica rufra*). It can be prepared in a number of ways—best, however, by heating oxalic acid with glycerine, when a mixture of formic acid and water distils over. The following reactions by which formates are produced synthetically are interesting:

$$(1) \qquad CO + HOK = HCOOK.$$
$$(2) \quad 2CO_{OH}^{OH} + 2K = CO_{OK}^{OH} + CO_{H}^{OK} + H_2O.$$
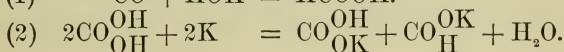
The first reaction takes place best at 200°, and the second occurs when potassium is suspended in moist carbon dioxide.

Anhydrous formic acid boils at 99°.9, forms crystals on cooling which melt at 8°.6. It has a sharp acid odor, and is painfully corrosive to the skin. It decomposes completely on warming with sulphuric acid into carbon monoxide and water.

Constitution of the Derivatives of Methane.

The first question regarding the constitution of methane is: Do the four atoms of hydrogen differ from each other in their relation to the atom of carbon? No satisfactory answer can be given: we can only say that there is as yet no evidence of any difference in the hydrogen atoms in CH_4. Methyl chlo-

ride, CH_3Cl, has been prepared in a number of different ways, and the different preparations have been found to possess identical properties. If there were a difference in the hydrogen atoms in CH_4 we might expect to obtain two or more isomeric methyl chlorides. We therefore consider all of the four hydrogen atoms to be similarly related or joined to the atom of carbon, and represent this view by the graphic formula

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H.$$
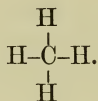
If one atom of hydrogen in methane is replaced by another univalent element, it can make no difference which one is replaced, since but one arrangement or linking of the atoms is possible. For example, methyl iodide may be represented by

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-I; \quad H-\overset{\displaystyle H}{\underset{\displaystyle I}{C}}-H; \quad H_3CI; \quad \text{or} \quad CH_3I.$$
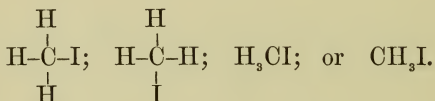
All the formulas indicate that three atoms of hydrogen and one of iodine are joined to one atom of carbon.

Methyl iodide is obtained from methyl alcohol, and, as shown later, the alcohol can be obtained from the iodide. Since methyl iodide contains the radical CH_3, we infer that methyl alcohol also contains the same radical, and that in methyl alcohol three atoms of hydrogen are linked to carbon. What relation does the atom of oxygen and the fourth atom of hydrogen bear to the carbon? The reactions by which methyl alcohol is formed from compounds of known constitution, and the reactions of the alcohol with other compounds, answer the question. Methyl iodide and potassium hydroxide react to form methyl alcohol:

$$H_3C-I + K-OH = H_3C-OH + K-I.$$
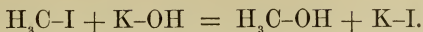
By acting on methyl alcohol with hydrogen chloride, OH can be replaced by Cl by a reaction analogous to that which occurs between potassium hydroxide and hydrogen chloride, thus:

$$H_3C-OH + H-Cl = H_3C-Cl + H_2O;$$

$$K-OH + H-Cl = K-Cl + H_2O.$$
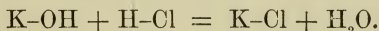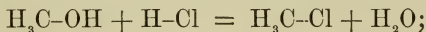
We conclude, then, that methyl alcohol contains the radicals CH_3 and OH, and that its graphic formula is

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\vert}}{C}-O-H.$$
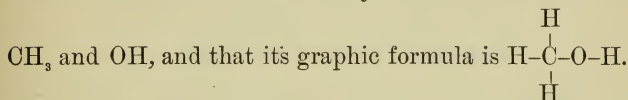
Since formaldehyde is derived from methyl alcohol by the removal of two atoms of hydrogen, and is converted into formic acid by the addition of one atom of oxygen, the natural inference is that the aldehyde contains the hydroxyl group which exists in both the alcohol and acid. This view is represented by the following formulas:

$$
H-\overset{\displaystyle H}{\underset{\displaystyle H}{\vert}}{C}-OH; \qquad
-\overset{\displaystyle H}{\underset{\displaystyle \vert}{C}}-OH; \qquad
O=\overset{\displaystyle H}{C}-OH.
$$

Methyl alcohol   Formaldehyde   Formic acid
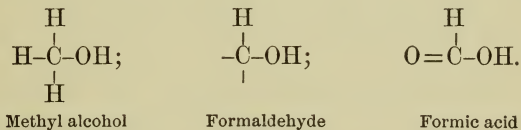
Aldehydes, however, do not exhibit the deportment of hydroxides. When acetaldehyde, for example, is treated with a chloride of phosphorus, the compound CH_3CCl is not formed, as would be the case if hydroxyl was replaced by chlorine; but the atom of oxygen is replaced by two atoms of chlorine, with formation of the compound CH_3CCl_2H, known as dichlorethane. If the aldehydes do not contain hydroxyl, we cannot represent formaldehyde by $-\overset{\displaystyle H}{\underset{\displaystyle \vert}{C}}-OH.$ The other possible for-

mula is $\begin{matrix} H \\ | \\ H-C=O. \end{matrix}$ If the constitutional formula of formalde-

hyde is written H–CHO, no view is expressed regarding the structure of the univalent group –CHO. This group is characteristic of the class of compounds known as aldehydes, which have the general formula R–CHO, R representing a univalent hydrocarbon radical. Thus, replacing R by methyl, CH_3, we have acetaldehyde, CH_3–CHO.

Aldehydes unite directly with oxygen to form acids:

$$HCHO + O = HCOOH;$$

$$CH_3CHO + O = CH_3COOH.$$
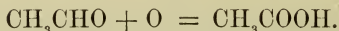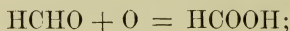
Formic acid has the empirical formula CH_2O_2. Since it is monobasic, containing but one atom of hydrogen replaceable by basic radicals with formation of salts, the two atoms of hydrogen do not bear the same relation to the atom of carbon. One hydrogen atom is supposed to be linked to carbon by one atom of oxygen. In other words, formic acid, in common with oxygen acids in general, contains hydroxyl. Since the other atoms of oxygen and of hydrogen are differently related to the carbon atom, each must be linked directly to the carbon atom, giving the structural formula $\begin{matrix} H-C-O-H \\ \| \\ O \end{matrix}$ for formic acid. The univalent group –COOH, containing the radicals carbonyl and hydroxyl, is called carboxyl. Later we shall learn that there are good reasons for supposing acetic acid to contain the carboxyl group, and to have a constitution similar to formic acid.

Compound Ammonias.

The hydrogen of ammonia may be partly or entirely replaced by hydrocarbon radicals with formation of a class of

bodies known as *amines*. If the replacing radical contains oxygen, and is acid in character, the resulting compound ammonia is called an *amide*. Carbamide, $CO < ^{NH_2}_{NH_2}$, may be viewed as formed by the replacement of hydrogen in two molecules of ammonia by the acid radical carbonyl, CO. Acetamide, CH_3CONH_2, contains the acid radical acetyl, CH_3CO, described later.

When methyl iodide is heated with an alcoholic solution of ammonia, the following reactions occur:

$$NH_3 + CH_3I = NH_2CH_3 + HI.$$
$$\text{Methylamine}$$
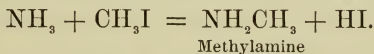
The methylamine exchanges an atom of hydrogen for CH_3:

$$NH_2CH_3 + CH_3I = NH(CH_3)_2 + HI.$$
$$\text{Dimethylamine}$$
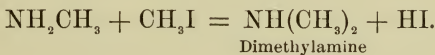
The reaction continues until all of the hydrogen is replaced by methyl:

$$NH(CH_3)_2 + CH_3I = N(CH_3) + HI.$$
$$\text{Trimethylamine}$$
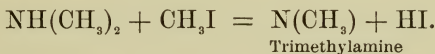
The trimethylamine combines with methyl iodide to form tetramethylammonium iodide:

$$N(CH_3) + CH_3I = N(CH_3)_4I.$$
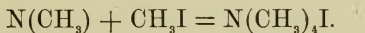
The hydriodic acid of the reactions combines with the ammonia used and the amines to form iodides.

Methylamine, NH_2CH_3, is a gas which liquefies at a few degrees above zero. It closely resembles ammonia in chemical properties and odor. It is more soluble in water than ammonia. Like the latter, it forms salts by direct union with acids.

For example, with hydrochloric acid it forms methylammonium chloride, NH_3CH_3Cl.

Dimethylamine, $NH(CH_3)_2$, is very similar to the preceding compound. It boils between 8° and 9°.

Trimethylamine, $N(CH_3)_3$, is not uncommon in nature, being found in a number of plants, in animal liquids, and especially in herring brine. It is obtained in quantity in the distillation of the "vinasses" or the waste liquids of the beet-sugar refineries. It boils between 9° and 10°, and has a strong, fish-like odor. It is used in the arts and in medicine.

Tetramethylammonium Iodide, $N(CH_3)_4I$, is the chief product of the reaction between methyl iodide and ammonia. It is a bitter-tasting, white crystalline salt. When freshly prepared silver oxide is added to its aqueous solution tetramethyl-ammonium hydroxide, $N(CH_3)_4OH$, is formed. This last compound is a crystalline solid, which is similar in properties to the fixed caustic alkalies. It forms salts with acids which are not decomposed by potassium hydroxide.

It will be observed that tetramethylammonium hydroxide is ammonium hydroxide with four atoms of hydrogen replaced by four methyl groups. One of the reasons for the formula NH_4OH is the existence of compounds like $N(CH_3)_4OH$.

Derivatives of Ethane.

These contain two atoms of carbon linked directly to each other, and are often called dicarbon compounds in distinction from derivatives of methane or monocarbon compounds. There are a number of ways by which dicarbon compounds can be formed synthetically from molecules containing only one atom of carbon. Such reactions are of the highest importance,

since they are the means not only of preparing complex compounds, but also give knowledge of their constitution.

Ethane, C_2H_6 or H_3C-CH_3. Gas density, 15.—This gas accompanies petroleum, and occurs in the gases of the natural gas wells. It is formed when methyl iodide and zinc are heated together at $150°$:

$$2CH_3I + Zn = C_2H_6 + ZnI_2.$$
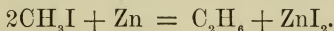
The zinc removes the iodine from two molecules of methyl iodide, and two methyl radicals unite to form one molecule of ethane. This synthesis leads to the constitutional formula

$$\begin{array}{cc} H & H \\ | & | \\ H-C-C-H. \\ | & | \\ H & H. \end{array}$$
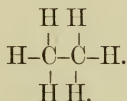
Ethane has also been obtained in other ways, and the various preparations have not been found to differ in properties. Hence the inference is that there are no isomers of C_2H_6. A different linking of the atoms than the one given is not conceivable in the present state of chemical science.

Chlorine replaces successively all of the hydrogen in ethane. The first stage of the reaction may be represented as follows:

$$\begin{array}{cccc} H & H & & H & H \\ | & | & & | & | \\ H-C-C-H & + Cl_2 = & H-C-C-Cl & + HCl, \\ | & | & & | & | \\ H & H & & H & H \end{array}$$
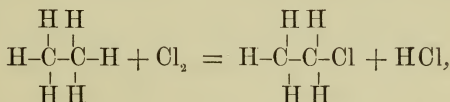
CH_3CH_2Cl is ethyl chloride. It is prepared by other methods, one of which is by acting on ethyl alcohol with hydrogen chloride:

$$C_2H_5-OH + HCl = C_2H_5-Cl + H_2O.$$
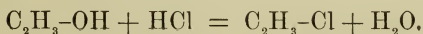
Ethyl chloride boils at 12°.5.   Ethyl bromide is similar to the chloride, and boils at 38°.4.

Methyl and ethyl belong to a class of hydrocarbon radicals which exist in alcohols, and such radicals are sometimes termed alcohol radicals. Thus, for example, in propyl alcohol, C_3H_7OH, the alcohol radical is C_3H_7.

Ethyl Iodide, C_2H_5I. Gas density, 78.—This compound is obtained by acting on ethyl alcohol with iodine and phosphorus, the reaction being analogous to that given for the formation of methyl iodide. Ethyl iodide is a colorless liquid, boiling at 72°, and having a density of 1.93. It is soluble in alcohol and ether, but almost insoluble in water. Like methyl iodide and many other organic iodides, it decomposes on exposure to light, with separation of iodine, which colors the liquid red.

It is especially adapted for the synthesis of ethyl compounds, as it readily exchanges iodine for metals and compound radicals. Experience has shown that iodine in organic compounds is more readily replaced than chlorine or bromine.

Exp. 223.—Place in a flask of about 800 cc. capacity 200 cc. of ordinary alcohol and 20 grams of red phosphorus, and then add gradually 200 grams of iodine. The mixture will become warm, and it may be necessary to cool it by allowing water to flow over the flask. After all of the iodine has been added, connect the flask with an upright condenser and allow to stand for a day. Then distil off the ethyl iodide, best by partly immersing the flask in a water-bath. The distillate contains ethyl iodide, water, alcohol, and a little hydriodic acid. The impure iodide is washed with water containing a little sodium hydroxide to remove the alcohol and acid, the former being taken up by the water and the latter by the alkali. In order to dry the iodide it is left in contact with calcium chloride for a day, without exposure to light. Finally, the ethyl iodide is poured off from the calcium chloride and distilled. For many purposes it is not necessary to dry and redistil the iodide before using.

Leave a small portion of the ethyl iodide exposed to light, and keep the remainder out of light.

Ethyl Alcohol, C_2H_5OH. —In the same way that methyl alcohol is derived from methyl iodide, ethyl alcohol may be derived from ethyl iodide. In place of potassium hydroxide 15 parts of water at 100° will answer :

$$C_2H_5I + HOH = C_2H_5OH + HI.$$
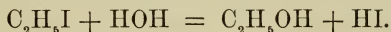
The radical ethyl has been shown to have the structure

$$H - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} -.$$ The above reaction leads then to the structural

formula $H - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - OH$ for ethyl alcohol, in which one hydrogen
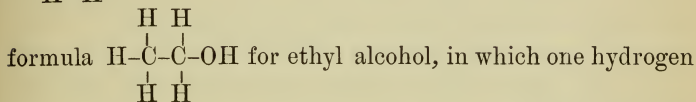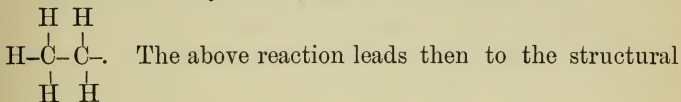
atom is linked by oxygen to one carbon atom; that is, the alcohol contains the hydroxyl group, and is ethyl hydroxide. Proof of the existence of the radical ethyl is found in a large number of the reactions of the alcohol by which ethyl is transferred to other combinations. Admitting the existence of ethyl in common alcohol, then the above structural formula is the only one possible. It is more conveniently written CH_3CH_2OH. It will be noticed that ethyl alcohol differs from methyl alcohol by CH_2. There is the same difference between ethane, C_2H_6, and methane, CH_4, and many of the derivatives of these hydrocarbons.

Ethyl alcohol is the best known of the alcohols, and is commonly called alcohol, and also, more rarely than formerly, spirits of wine. It is the basis of intoxicating beverages, which have been manufactured in all ages and by all nations from cereals and fruits. The juices of fruit contain sugar, which is converted into alcohol by fermentation. The cereals and potatoes are largely composed of starch, which is first transformed into a sugar, and this in turn yields alcohol when fermented. The alcohol is separated from the non-volatile products of the fermented liquid by distillation. The crude spirit obtained

from cereals or potatoes contains a large proportion of water and small quantities of a number of organic compounds. By repeated rectification and filtering through charcoal a spirit is obtained containing 90 to 96 per cent of pure alcohol, the remainder being water. All the water cannot be separated from alcohol by distillation. To remove the water in common alcohol, the latter is left in contact for some time with lime, potassium carbonate, or some other compound which takes up water, absolute alcohol being finally distilled off.

Absolute alcohol boils at $78°.4$, and has a density at $15°$ of 0.794. It is very hygroscopic, and mixes in all proportions with water. It burns with a pale-blue flame. Next to water, alcohol is the most common solvent, dissolving fats, oils, resins, and other kinds of carbon compounds, and also some inorganic salts.

Alcohol is used for a great variety of purposes in the industrial arts. It is indispensable in the preparation of many medicines, and in the laboratory.

Aldehyde or Acetaldehyde, CH_3CHO, is derived from alcohol by taking out two atoms of hydrogen:

$$CH_3CH_2OH + O = CH_3CHO + H_2O.$$
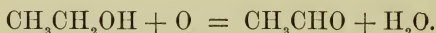
Various oxidizing agents effect the change. Aldehyde is also formed when a mixture of sodium formate and sodium acetate is heated, thus:

$$\begin{matrix} HCOONa \\ CH_3COONa \end{matrix} = CH_3CHO + Na_2CO_3.$$

Both reactions serve for the preparation of other aldehydes.

Acetaldehyde boils at $20°.8$, giving off a vapor with a peculiar irritating odor. It mixes in all proportions with water and alcohol. Small quantities of inorganic acids convert aldehyde into a polymeric compound called *paraldehyde,*

$C_6H_{12}O_3$, boiling at 124°, and possessing a gas density corresponding to the molecular formula given. Aldehyde readily unites with oxygen to form acetic acid. A mixture of aldehyde, ammonia, and silver nitrate deposits a mirror of silver on warming. The reaction serves to detect traces of aldehyde.

Acetic Acid, CH_3COOH.—This di-carbon compound can be formed synthetically from a monocarbon compound as follows. Methyl iodide and potassium cyanide react when heated together to form potassium iodide and methyl cyanide or acetonitrile, thus:

$$H_3CI + K-C \equiv N = H_3C-C \equiv N.$$

Acetonitrile on warming with potassium hydroxide yields acetic acid and ammonia, thus:

$$H_3C-C \equiv N + 2H_2O = H_3C-CO_2H + NH_3.$$
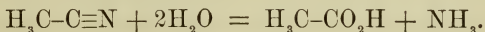
It will be observed that the constitution thus far derived for acetic acid is based upon that assigned to methyl cyanide, in which it is assumed that the two carbon atoms are directly linked. This view is supported by the deportment of methyl isocyanide,* $H_3C-N \equiv C$, which is decomposed with difficulty by alkalies, but is converted by acids into two monocarbon compounds, thus:

$$H_3C-N \equiv C + 2H_2O = H_3C-NH_2 + HCOOH.$$
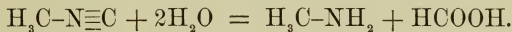
The difference in deportment of the two methyl cyanides is best explained by the theory that the carbon atoms in one are linked together and are not in the other. If the structural formula of acetonitrile is correct, then in all probability the two carbon atoms are linked together in acetic acid, and we

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* Methyl isocyanide is obtained by acting on methyl iodide with silver cyanide. It boils at 58° to 59°. Methyl cyanide boils at 82°.

must next discuss the relation of the four atoms of hydrogen and two of oxygen to the carbon atoms. The radical CH_3 was transferred from CH_3I to CH_3CN, and we may assume that CH_3 remains unchanged when methyl cyanide is converted into acetic acid. The fourth atom of hydrogen and the two atoms of oxygen and one atom of carbon form a group united to CH_3. Regarding carbon as tetravalent and oxygen as bivalent, we see, if our theory thus far is correct, that there are two possible formulas for acetic acid, viz.:

$$\text{(1)} \quad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-C\underset{O}{\overset{O}{\diagup}}\cdot \qquad \text{(2)} \quad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-H.$$
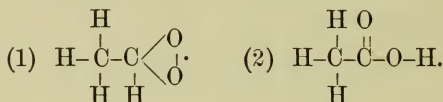
It has already been shown that oxygen acids when treated with phosphorus trichloride or pentachloride exchange hydroxyl for chlorine. Acetic acid by similar treatment yields acetyl chloride, thus:

$$3CH_3CO_2H + PCl_3 = 3CH_3COCl + P(OH)_3.$$
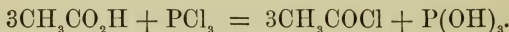
And acetyl chloride with water yields acetic acid:

$$CH_3CO \, \overline{|\, Cl + H \,|} \, OH = CH_3COOH + HCl.$$
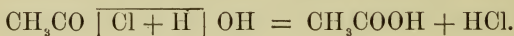
These reactions show that acetic acid contains one hydroxyl group, and that its properties are best represented by the formula

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-H.$$
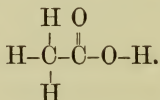
The shorter formula CH_3COOH embodies the same view. Acetic acid, as its formula indicates, is monobasic. Acetyl, CH_3CO, is the acid radical of acetic acid.

Alcohol is converted by oxidizing agents first into aldehyde and then into acetic acid. Alcohol is unchanged by pure air unless in contact with platinum black; but fermented liquors, containing nitrogenous matter, become sour on exposure to air unless too large a proportion of alcohol is present. The sour product is vinegar, which is a very dilute solution of acetic acid, and contains small quantities of other compounds, imparting color and flavor. The formation of vinegar from dilute alcoholic solutions is due to the growth of a microscopic organism (*Mycodermi aceti*), which in some way serves as a carrier of atmospheric oxygen. Vinegar is manufactured from many different substances, such as poor wines, cider, and malt. The formation of vinegar is hastened by addition of "mother of vinegar," which contains *Mycodermi aceti*, and also by allowing the liquor to flow through a mass of shavings in which air circulates.

Another considerable source of acetic acid is the liquid product of the distillation of wood. This contains, among other compounds, acetic acid. The acid is neutralized with lime or soda, and the salt, which remains after evaporation, is heated to remove impurities. The sodium or calcium acetate is mixed with sulphuric acid, and the acetic acid is distilled off.

Pure acetic acid is a colorless liquid, boiling at 119°. Its gas density is 45 at 125°. The density gradually diminishes with increasing temperature, and at 250° is 30, the density corresponding to the formula $C_2H_4O_2$. Acetic acid when cooled forms large transparent crystals melting at 16°.7. The presence of a small quantity of water lowers the melting point considerably. The acid which crystallizes on cooling is known as glacial acetic acid. It cannot be separated from dilute solutions by distillation, but is prepared by acting on anhydrous sodium acetate with sulphuric acid:

$$2CH_3COONa + SO_2{<}^{OH}_{OH} = 2CH_3COOH + SO_2{<}^{O-Na}_{O-Na}.$$
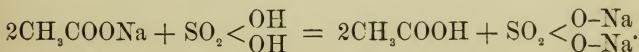
The acetic acid which is distilled off contains a little water. To prepare anhydrous acid ordinary glacial acetic acid is cooled until a considerable mass of crystals is formed. The liquid portion, containing more water than the crystals, is poured off. By repeating the process a number of times anhydrous acetic acid is obtained.

Glacial acetic acid is very stable. It is not readily decomposed by heat, nor is it oxidized by chromic acid. It is a valuable solvent for many organic compounds.

Sodium Acetate, CH_3COONa, is prepared by neutralizing dilute acetic acid with sodium carbonate. The solution on evaporation yields crystals of the hydrated salt, $CH_3COONa + 3H_2O$. The crystals lose their water on heating, and the anhydrous salt fuses without decomposition at 319°. Sodium acetate is used for the preparation of acetyl compounds.

Potassium Acetate, CH_3COOK, is a very deliquescent and soluble salt. It is used in medicine.

Calcium Acetate, $\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} > Ca$, is an easily soluble salt, crystallizing with two molecules of water.

Copper Acetate, $\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} > Cu$, is prepared by dissolving copper hydroxide or carbonate in acetic acid. It forms blue crystals containing one molecule of water. *Verdigris* is a basic copper acetate formed by the combined action of air and acetic acid on copper. It is employed in dyeing. It is very poisonous

Silicon, Si.

Atomic Weight, 28.   *Density,* 2.49.

This element occurs in silicon dioxide, SiO_2, or quartz, and in the numerous silicates, which, together with quartz, constitute most of the rocks, excepting limestones. Silicon is, next to oxygen, the most abundant element in the crust of the earth.

Amorphous silicon is obtained by heating a mixture of potassium silicon fluoride and metallic potassium :

$$K_2SiF_6 + 4K = Si + 6KF.$$
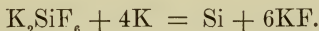
The potassium fluoride is dissolved by water, and the silicon is left as an amorphous brown powder, which burns readily when heated in air to silicon dioxide.

If the reduction is made with aluminum, and this metal is dissolved out of the metallic product by hydrochloric acid, silicon will be obtained in dark hexagonal tablets resembling graphite.

Crystalline silicon is also prepared by the following process. A mixture of potassium silicon fluoride, zinc, and metallic sodium is thrown into a red-hot crucible, and kept hot for some time, but not hot enough to volatilize the zinc. After cooling, the product is treated successively with hydrochloric, hot nitric, and hydrofluoric acids, when dark octahedral crystals of silicon will remain.

Quartz is reduced in the electrical furnace and silicon is obtained in a crystalline condition. If the reduction is made in the presence of copper this metal dissolves the silicon. The addition of a small proportion of silicon to some metals and alloys increases their tensile strength.

Silicon may be fused in a crucible and cast into bars. The crystalline form, when heated in oxygen, becomes coated with oxide, which protects it from further oxidation. Silicon dis-

solves in a boiling solution of potassium hydroxide, with evo-
lution of hydrogen and formation of potassium silicate.

Silicon Tetrahydride, SiH_4. Gas density, 16.—Pure silicon
tetrahydride is obtained by treating the compound $SiH(OC_2H_5)_3$
with sodium. The colorless gas thus prepared does not ignite
spontaneously at ordinary temperature, but does so when
mixed with hydrogen or when slightly warmed. When an
alloy of silicon and magnesium is treated with hydrochloric
acid, silicon tetrahydride together with hydrogen is evolved,
and the gas thus obtained ignites spontaneously on escaping
into the air, and burns with formation of a cloud of silica.
Silicon tetrahydride is the analogue of methane, CH_4.

Silicon Tetrafluoride, SiF_4. Gas density, 52.—This com-
pound is formed when hydrofluoric acid comes into contact
with silica :

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$
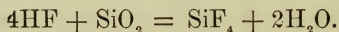
The water formed in the reaction decomposes the silicon
tetrafluoride as stated under Hydrogen Silicon Fluoride.

Pure silicon tetrafluoride is best prepared by heating a mix-
ture of fluor spar (calcium fluoride), sand, and sulphuric acid:

$$2CaF_2 + 2H_2SO_4 + SiO_2 = SiF_4 + 2CaSO_4 + 2H_2O.$$
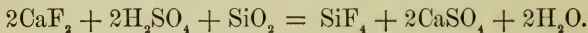
An excess of concentrated sulphuric acid is used to take up
the water formed.

Silicon tetrafluoride is a pungent colorless gas, fuming in
moist air. It combines with dry ammonia to form a white
compound having the composition $SiF_4.2NH_3$. This sub-
stance is completely dissociated at high temperatures into sili-
con tetrafluoride and ammonia.

Hydrogen Silicon Fluoride or Hydrofluosilicic Acid, H_2SiF_6. —This acid is formed when silicon fluoride is passed into water, silicic acid at the same time separating :

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4.$$

The saturated solution of hydrofluosilicic acid is a strongly acid fuming liquid, which leaves no residue when evaporated in a platinum dish, since the acid is decomposed on heating into silicon tetrafluoride and hydrofluoric acid.

A solution of hydrofluosilicic acid is used as a reagent for barium, precipitating the metal as barium silicofluoride, $BaSiF_6$, when added to a solution of a barium salt.

Exp. 224.—*a.* Place a mixture of equal parts of fluor spar and quartz sand in a flask containing 9 parts of oil of vitriol. Connect the flask by means of glass and rubber tubing with a delivery-tube, having a diameter of a centimeter or more, and which dips under mercury in a cylinder. Heat the flask cautiously with a lamp. Silicon fluoride will escape and fume in the air. Pour water into the cylinder. Each bubble of gas on entering the water will be surrounded by a film of gelatinous silica. After a time the gas will escape through channels formed. These should be broken up by stirring.

Filter the solution of hydrofluosilicic acid through cloth.

b. Add some hydrofluosilicic acid to a concentrated solution of barium chloride. Barium silicon fluoride will be precipitated.

c. Dry the gelatinous silica, and heat intensely in a crucible. The light white powder obtained is pure silica.

Silicon Tetrachloride, $SiCl_4$. Gas density, 84.8.—This substance is a colorless fuming liquid, boiling at 59°.6. It is formed by the direct union of silicon and chlorine, but is best prepared by passing chlorine through a mixture of silica and charcoal heated intensely in a porcelain tube:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$
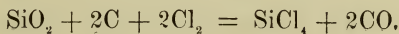
Silicon tetrachloride is quickly decomposed by water, with separation of gelatinous silica:

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$
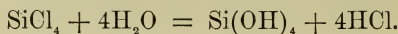
Silicon Trichloride, Si_2Cl_6. Gas density, 134.2.—This compound is obtained when the tetrachloride is passed over white-hot silicon. It is a mobile colorless liquid, solidifying at $-1°$, and boiling at $146°$.

Silicon Chloroform, $SiHCl_3$. Gas density, 68.—This body is an analogue of chloroform, $CHCl_3$. It is formed when silicon is heated in dry hydrochloric acid gas.

Silicon Dioxide or Silica, SiO_2, occurs in a great variety of forms. As quartz it is found in transparent colorless hexagonal crystals, terminated with six-sided pyramids. Quartz has a hardness of 7, and a density of 2.6. The varieties of native silica, on account of their peculiarities, are divided into three series, viz., the vitreous variety, having a glassy fracture; the chalcedonic, having a semi-vitreous and waxy lustre, and translucent; the jaspery, having little or no lustre, and opaque.

Among the vitreous varieties are the pure transparent colorless quartz or rock crystal, smoky quartz, common quartz sand, the amethyst, rose quartz, and milky quartz, the latter occurring in rock masses nearly opaque white. The amethyst has a purple or bluish-white color, due to traces of manganese, and is valued as a gem. Rose quartz is pink or rose-colored. Its color fades on exposure to light.

The chalcedonic varieties include chalcedony, agate, carnelian, onyx, and flint.

With the jaspery varieties are classed the various kinds of jasper, the bloodstone, touchstone, silicified or petrified wood, and some kinds of quartz sandstone.

Opal is an amorphous form of silica, usually containing a little water. It is not quite as hard as quartz. The finer varieties are much esteemed as gems. To this variety of

silica belongs infusorial earth which consists mainly of the silicious remains of microscopic plants. It is used for polishing, and for mixing with nitro-glycerine in the manufacture of dynamite.

Silica fuses in the oxyhydrogen flame to a clear glass. It is insoluble in water and acids excepting hydrofluoric. Amorphous silica is soluble in solutions of potassium and sodium hydroxides and carbonates; but crystalline silica is almost insoluble in these solutions. When either form is fused with an alkali hydroxide or carbonate a soluble alkali silicate is obtained.

Silicon Hydroxides or Silicic Acids.—When hydrochloric acid is added to a not too dilute solution of an alkali silicate a gelatinous mass separates, which is perhaps orthosilicic acid, $Si(OH)_4$, but which, on drying at ordinary temperatures, leaves no well-defined hydroxide or hydrate. If a dilute solution of an alkali silicate is poured into hydrochloric acid a clear solution results. The alkali salt may be removed by dialysis and a solution obtained containing 5 per cent of silica, and which may be concentrated by boiling in a flask until it has 14 per cent of silica. The solution on standing changes to a transparent jelly.

Exp. 225.—*a.* Pour a few cubic centimeters of a solution of sodium silicate (commercial water glass will answer) into an excess of hydrochloric acid in a porcelain dish; mix thoroughly by stirring, and evaporate to dryness—best on a water-bath. Moisten the residue with hydrochloric acid, add water to dissolve the sodium chloride, and wash the silica thoroughly on a filter with hot water. The silica after drying contains a little water, which may be driven off by ignition.

b. Try to dissolve a portion of the silica in hydrochloric acid, and another portion in a solution of potassium hydroxide.

c. Dilute sodium silicate with water until the solution does not gelatinize on pouring into hydrochloric acid. Fill a test-tube with the acid solution and set aside. If not too dilute, silicic acid will separate as a jelly in a few days. Evaporate on a water-bath the remainder of the solution of silicic acid until a jelly forms.

Silicates.—The greater number of silicates occur as minerals. But few silicates have been prepared in a state of purity. The observed gas densities of ethyl orthosilicate,

$$Si \begin{cases} O-C_2H_5 \\ O-C_2H_5 \\ O-C_2H_5 \\ O-C_2H_5 \end{cases}, \text{ and of ethyl metasilicate, } SiO \begin{cases} O-C_2H_5 \\ O-C_2H_5 \end{cases},$$
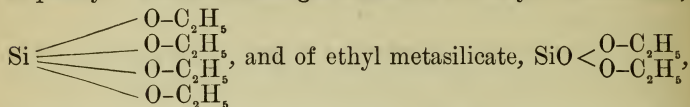
correspond to the formulas given. These compounds show the tetravalent character of silicon in silicates. Many silicates may be viewed as derivatives of polysilicic acids formed by the dehydration of two or more molecules of orthosilicic acid, thus:

| | Hexbasic disilicic acid. | Tetrabasic disilicic acid. | Dibasic disilicic acid. |

| | Octobasic trisilicic acid. | Hexbasic trisilicic acid. | Tetrabasic trisilicic acid. | Dibasic trisilicic acid. |
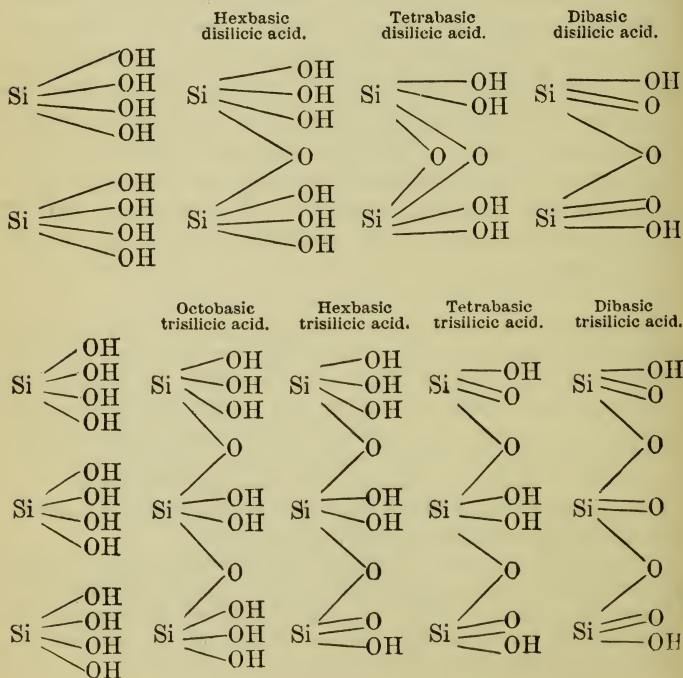
Sodium Silicates.—When a mixture of equal molecules of silica and sodium carbonate is fused, sodium metasilicate, Na_2SiO_3, is formed. It is soluble in water, and separates in hydrous crystals when the solution is evaporated. If an excess of sodium carbonate is used, sodium trisilicate, $Na_8Si_3O_{10}$, is obtained. Commercial silicate of soda, known also as water glass and soluble glass, is a mixture of sodium silicates, consisting chiefly of sodium tetrasilicate, $Na_2Si_4O_9$. It is manufactured by heating together 180 parts of sand, 100 of soda-ash, and 3 of charcoal. The glassy mass which results dissolves slowly in boiling water, forming a viscid alkaline liquid. Soluble glass is used with fresco colors, as a cement for mending broken porcelain and stone-ware, and in large quantities in the manufacture of silicated soaps.

Potassium Silicates resemble the sodium silicates, but are less used on account of the high cost of the potash required for their manufacture.

Glass is valued chiefly for its transparency and durability. There is no substitute for window glass. It protects from the weather and admits sunlight, which not only renders dwellings cheerful, but acts also as a purifying agent. Light, too, makes filth conspicuous. Glass was used by the ancients, but cheap glass for the multitude came with the great development of the chemical industries in the present century.

Glass is a mixture of silicates of metals belonging to two different groups. The ordinary kinds of glass are composed of alkali silicates and calcium or lead silicate. The alkali silicates are glassy in appearance after fusion, but are soluble in water. The calcium and lead silicates are practically opaque, and are decomposed by acids. But when sodium silicate and calcium silicate are melted together, a glass is formed which is not soluble in water, and is not corroded by acids, excepting hydrofluoric acid.

Window or crown glass is made by melting in a fire-clay pot a mixture of sand, soda-ash, and lime or limestone. Broken glass (cullet) is also added to facilitate the melting. Arsenic trioxide and manganese dioxide are used in small quantities to counteract color imparted by iron contained in the ingredients. Window glass consists of 70 to 75 per cent of SiO_2, and from $12\frac{1}{2}$ to 15 per cent each of Na_2O and CaO.

Flint or crystal glass is composed of potassium and lead silicates. It is characterized by its high density, brilliant lustre, and great refracting power. It is more fusible than other kinds of glass, and does not resist the action of chemicals as well. It is used for the finer kinds of glass-ware, and for optical purposes.

Bohemian or hard glass is a potassium calcium silicate. It is valuable for its infusibility and resistance to chemicals.

Common green bottle glass is similar in composition to window glass, but contains aluminum and iron derived from the impure and cheap materials used in its manufacture. The green color of bottle glass is due to iron.

The brittleness of glass, and its property of gradually softening and becoming pasty when heated, are familiar to chemical students, and need not be described. Glass is slowly acted upon by water ; some saline solutions dissolve it to a greater extent, and alkaline solutions corrode it still more. Hence many exact chemical experiments must be made in platinum instead of glass dishes.

Water from steam condensed in glass will leave more residue on evaporation than if condensed in a block-tin or platinum tube.

Clay.—Kaolin, the purest kind of clay, is a hydrous aluminum silicate. It has been formed by the decomposition of aluminous minerals, especially the feldspars, which are silicates of aluminum and sodium or potassium, often containing small amounts of other metals. Common clays are composed

of kaolin mixed with powdered feldspar, quartz, or other minerals. Clays are distinguished by forming a plastic mass with water, which becomes hard and compact when intensely heated. The properties of different clays will be noticed in connection with articles manufactured from them.

Porcelain is made by mixing fine white kaolin with sufficient pulverized quartz and feldspar so that the mass will partly fuse when heated and become translucent. The ware is next coated with a more fusible mixture, which on heating forms the smooth, glass-like surface of porcelain.

Common Earthen and Stone Ware are made from the common varieties of clay. Both kinds of ware before glazing are porous and opaque.

Bricks are of two kinds, common building brick and fire-brick. The former are often red from oxide of iron contained in the clay. Fire-brick are made by mixing fire-clay with pulverized and previously burned fire-clay to prevent cracking on drying. Fire-brick are used for stove and furnace linings. The crucibles used in metallurgical processes, and the pots in which glass is melted, are made of the most refractory fire-clay.

Hydraulic Mortar or Cement.—Limestone containing 10 per cent or more of clay is converted by burning into a mass, which in state of fine powder possesses the property of hardening under water. The chemical change which occurs in the hardening is not well understood. It has been supposed that an insoluble hydrous calcium aluminum silicate is formed, and also that the calcium aluminate contained in the cement takes up water. Some cements, containing little silica and alumina, require weeks to harden ; others made from hydraulic limestone containing 25 to 35 per cent of clay begin to harden

soon after wetting, and become firm in a few hours. Cement is obtained not only from hydraulic limestones, but also by calcining a mixture of chalk or limestone and clay.

Titanium, Ti.

Atomic Weight, 48.

Titanium occurs in nature as dioxide, and is also found in some iron ores and silicates. It is a comparatively rare element. Metallic titanium is obtained by reducing potassium titanium fluoride with potassium. On dissolving the fused mass in water the titanium remains as an amorphous powder, which burns brilliantly in air, is soluble in acids, and decomposes boiling water. According to Kern, the latter reaction is due to potassium contained in the product. Crystals of titanium are formed when vapor of titanium chloride is passed over molten sodium.

Titanium Dichloride, $TiCl_2$, is formed by heating the higher chlorides in a current of hydrogen. It is a hygroscopic brown powder, which decomposes water.

Titanium Trichloride, $TiCl_3$, is obtained in dark-violet scales when the vapor of titanium tetrachloride and hydrogen are passed together through a red-hot tube. It is non-volatile, and decomposes at high temperatures into $TiCl_2$ and $TiCl_4$. It is deliquescent, and yields a violet solution with water.

A solution prepared by dissolving metallic titanium in hydrochloric acid deposits on evaporation crystals of the hydrated trichloride, $TiCl_3 + 4H_2O$. During the evaporation titanic acid separates, and the solution must be frequently filtered.

Titanium trichloride is a strong reducing agent, separating sulphur from sulphur dioxide.

Titanium Tetrachloride, $TiCl_4$, is formed by heating titanium in chlorine, and by passing chlorine over a mixture of titanic oxide and charcoal. It is a colorless liquid, boiling at 136°, having a gas density corresponding to the formula $TiCl_4$.

Titanium tetrachloride is soluble in cold water, and forms in moist air a soluble hydrate. The aqueous solution, on heating and evaporating, decomposes into titanic and hydrochloric acids.

Titanium Tetrafluoride, TiF_4.—When a mixture of fluor spar, titanic oxide, and fuming sulphuric acid is distilled, titanium tetrafluoride is obtained as a colorless fuming liquid.

Hydrogen Titanium Fluoride, H_2TiF_6, is formed when titanic oxide is dissolved in hydrofluoric acid.

Potassium Titanium Fluoride, K_2TiF_6, is prepared by neutralizing hydrogen titanium fluoride with potassium hydroxide, and also by fusing titanic oxide with potassium carbonate and dissolving the fused mass in boiling dilute hydrofluoric acid. On cooling, the potassium salt separates in scales which melt without decomposition.

Titanium Sesquioxide, Ti_2O_3, is prepared by igniting the dioxide in a current of hydrogen. It is soluble in sulphuric acid, forming a violet solution.

Titanium Dioxide or Titanic Oxide, TiO_2, occurs as rutile in tetragonal crystals, density 4.18-4.25; as octahedrite (anatase); also in tetragonal crystals of totally different form, having a density of 3.82-3.95; and as brookite in orthorhombic crystals, density 4.12-4.23. Amorphous titanium dioxide is prepared by igniting titanium hydroxide. It is a white powder, insoluble in water, hydrochloric and dilute sulphuric acids, but dissolves in hydrofluoric acid and concentrated sulphuric acid.

The amorphous dioxide is converted into crystals of octahedrite at about 860°; into crystals of brookite at about 1000°; and at still higher temperatures into crystals of rutile.

Titanic Acids.—Titanium forms two hydroxides, which are called titanic and metatitanic acids. According to some authorities, both acids have the composition $Ti(OH)_4$, while others assign the formula $TiO(OH)_2$. Both acids lose water with increasing temperature, and finally leave TiO_2.

Titanic acid is obtained by adding an alkali hydroxide to a cold solution of titanic chloride. It is soluble in hydrochloric, dilute sulphuric, and nitric acids, and the solution on boiling deposits metatitanic acid, which is insoluble in acids except hydrofluoric and concentrated sulphuric. Metatitanic acid is also obtained by dissolving titanic oxide in sulphuric acid, diluting the solution with a large quantity of water, and then boiling.

The titanium hydroxides act as weak bases, and also as acids forming salts both with acids and bases, but the compounds are not well understood. The following formulas illustrate the complex composition of titanates: $K_2TiO_3 + 4H_2O$, $K_2Ti_3O_7 + 2H_2O$, $K_2Ti_6O_{13} + 2H_2O$, and $K_2Ti_3O_7 + 3H_2O$. The iron titanates are even more complex.

Titanium Sesquisulphate or Titanous Sulphate, $Ti_2(SO_4)_3 + 8H_2O$, is

formed by dissolving titanium in sulphuric acid. The violet solution on concentration becomes blue, aud deposits crystals of the salt.

Titanium Bisulphate or Titanic Sulphate, Ti(SO$_4$)$_2$ + 3H$_2$O, is obtained as a yellow amorphous mass when titanous sulphate is treated with nitric acid and a few drops of sulphuric acid, and the solution is evaporated.

Titanyl Sulphate, TiOSO$_4$, is obtained by dissolving titanic oxide in boiling sulphuric acid and evaporating the solution.

Titanium Nitrides.—The compound Ti$_3$N$_4$ results when titanium tetrachloride and ammonium chloride are heated together. By passing dry ammonia over red-hot titanic oxide the mono nitride TN is formed.

Titanium Cyano-nitride, Ti(CN)$_2$.3Ti$_3$N$_2$, is formed in blast furnaces in the smelting of titaniferous iron ores, and is found in the slag and pig iron as copper-colored scales. It is also formed when titanic oxide and charcoal are intensely heated in a crucible, the nitrogen being supplied by the air

Zirconium, Zr.

Atomic Weight, 90.7.   *Density,* 4.15.

The oxide of zirconium was discovered by Klaproth in 1789 in the mineral zircon, ZrSiO$_4$. The metal was first isolated by Berzelius, who obtained it in the form of an amorphous dark powder by reducing potassium zirconium fluoride with potassium. Crystalline gray scales of the metal are obtained when the reduction is made with aluminum. Crystalline zirconium is brittle, very hard, and infusible. It does not oxidize at a red heat, but at a white heat becomes coated with oxide, which protects it from further oxidation. It is soluble in aqua regia and in hydrofluoric acid.

Zirconium Chloride, ZrCl$_4$, is prepared by heating an intimate mixture of zirconium oxide and charcoal in a current of chlorine. It forms a white sublimate. Its observed gas density is 117; theory for ZrCl$_4$ is 115.5. Its aqueous solution loses hydrochloric acid when evaporated, and deposits hydrous crystals of zirconyl chloride, ZrOCl$_2$. The same compound is also formed when zirconium hydroxide is dissolved in hydrochloric acid

Zirconium Fluoride, ZrF$_4$, is obtained by heating zirconium oxide with acid ammonium fluoride. A solution of the fluoride in hydrofluoric acid yields crystals of ZrF$_4$ + 3H$_2$O, which decompose on drying, and at a red heat leave zirconium oxide.

Potassium Zirconium Fluoride, K_2ZrF_6, is prepared by fusing zircon with acid potassium fluoride, or by adding potassium fluoride to an excess of a solution of zirconium fluoride. It is very soluble in hot and sparingly soluble in cold water.

Zirconium Oxide or Zirconia, ZrO_2, is obtained as a white powder by igniting the hydroxide. When zirconia is intensely heated with borax, crystals are formed which are isomorphous with cassiterite and rutile.

Zirconium Hydroxide, $Zr(OH)_4$, separates as a gelatinous white precipitate on addition of ammonia to a cold solution of the sulphate or chloride. The washed precipitate after drying at 17° has the composition $Zr(OH)_4$ (Hermann). Berzelius found that it corresponded to $ZrO(OH)_2$, probably after drying at a higher temperature. Zirconium hydroxide when precipitated cold is easily soluble in hydrochloric acid, but when precipitated hot is difficultly soluble. It is insoluble in alkali hydroxides. Zirconium hydroxide is both acidic and basic, as the zirconates and zirconium sulphate show.

Zirconates.—Sodium metazirconate, $ZrO{<}^{O-Na}_{O-Na}$, is formed when a mixture of zirconia and sodium carbonate is fused. If the fusion is kept at a white heat for some time sodium orthozirconate, $Zr{<}^{O-Na}_{O-Na}{}^{O-Na}_{O-Na}$, is formed.

Zirconium Sulphate, $Zr(SO_4)_2$, is obtained by evaporating a solution of the oxide or hydroxide in sulphuric acid, and heating the residue nearly to redness. A solution of the sulphate saturated with zirconium hydroxide, yields on evaporation zirconyl sulphate, $ZrOSO_4$.

Cerium, Ce.

Atomic Weight, 141.   *Density,* 6.6.

This element was discovered in 1803 by Klaproth, and independently by Berzelius and Hisinger. It occurs associated with lanthanum and didymium in a few rare minerals. The metal is obtained by electrolyzing the chloride. It has the color and lustre of iron, is tolerably permanent in dry air, and in moist air becomes first yellow, then blue, and finally green. Its melting point is below that of silver. Cerium burns in air with greater brilliancy than magnesium. It is soluble in acids.

Cerium forms two classes of compounds, viz., the cerous, in which cerium is trivalent; and the ceric, in which it is tetravalent.

Cerous Chloride, $CeCl_3$, is formed when the metal is heated in chlorine. A solution of cerous oxide in hydrochloric acid on evaporation deposits crystals of $CeCl_3 + 5H_2O$, which on heating give off hydrochloric acid and change to a basic salt.

Cerous Oxide, Ce_2O_3, is obtained by igniting the carbonate or oxalate in pure hydrogen. It is a bluish powder, which quickly oxidizes in air to dioxide. Sodium hydroxide precipitates from solutions of cerous salts a hydroxide which absorbs oxygen and carbon dioxide from the air.

Cerous Sulphate, $Ce_2(SO_4)_3$, is prepared by dissolving cerous oxide or carbonate in sulphuric acid. It is very soluble in cold and only slightly soluble in hot water. This phenomenon is explained by the existence of different hydrates of the salt which differ in solubility.

Cerous Carbonate, $Ce_2(CO_3)_3 + 9H_2O$, forms a bulky precipitate when ammonium carbonate is added to a solution of cerous sulphate.

Ceric Oxide or Cerium Dioxide, CeO_2, is formed when a cerium salt of a volatile acid is ignited in air. It dissolves in hydrochloric acid, and the solution on heating evolves chlorine, and cerous chloride is formed.

Ceric Sulphate, $Ce(SO_4)_2$, has been obtained in hydrous crystals. A solution of ceric oxide in sulphuric acid evolves ozone, and contains cerous sulphate and ceric sulphate.

Thorium, Th.

Atomic Weight, 232. *Density,* 11.

The oxide of this metal, thoria, was discovered in 1829 by Berzelius in a mineral now known as thorite, a thorium silicate. Thorium occurs in a few other rare minerals. Nilson isolated the metal by the following process. A mixture of dry potassium thorium chloride, sodium chloride, and metallic sodium was heated to redness in an iron crucible closed by a cover held by a clamp. The contents of the crucible after cooling were treated with water to dissolve the salts, and also the metallic sodium remaining. The thorium which remained was washed with alcohol and ether, and dried at 100°. The metal thus obtained was in the form of a gray crystalline, brittle powder, which ignited in air below redness and burned brilliantly to a snow-white oxide. It has not been fused. It is soluble in concentrated hydrochloric acid, but is not attacked by solutions of alkali hydroxides.

Thorium Chloride, ThCl$_4$, is prepared by heating the metal in chlorine, and also in hydrogen chloride. Vapor density found, 178; theory for ThCl$_4$, 187. A solution of the chloride is obtained by dissolving the hydroxide in hydrochloric acid.

Thorium Dioxide, ThO$_2$, remains as an amorphous powder when the hydroxide is ignited. On heating the powder intensely with borax, it changes to crystals which are isomorphous with crystals of the compounds SnO$_2$, ZrO$_2$, and TiO$_2$.

Thorium Hydroxide, Th(OH)$_4$, separates on addition of ammonia to a solution of thorium chloride. It absorbs, when moist, carbon dioxide. It does not appear to possess acidic properties.

Thorium Sulphate, Th(SO$_4$)$_2$, is prepared by dissolving the oxide in hot sulphuric acid, and then expelling the excess of acid by heat. It is soluble in water, and forms several hydrates.

Germanium, Ge.

Atomic Weight, 72. *Density,* 5.5.

This element was discovered in 1886 by Winkler in a mineral found in the mines at Freiberg, in Saxony. Metallic germanium is obtained by heating the oxide in hydrogen. It melts at about 900°, has a grayish-white color, exhibits a beautiful metallic lustre, and crystallizes in regular octahedrons. It is insoluble in hydrochloric acid, soluble in aqua regia, and is converted into oxide by nitric acid. It is a tetrad, forming, however, compounds in which it is a dyad.

Germanium Dichloride, GeCl$_2$, is probably formed when the monosulphide is heated in hydrogen chloride. It has not been obtained in the pure state.

Germanium Tetrachloride, GeCl$_4$, results from the direct combination of its elements. It is a colorless liquid, boiling at 86°. At −100° it does not solidify. Gas density found, 107.4; calculated for GeCl$_4$, 106.8.

Germanium Chloroform, GeHCl$_3$, is prepared by heating the metal in hydrogen chloride. It is a colorless mobile liquid, which absorbs oxygen from the air with formation of oxychloride, GeOCl$_2$(?), and evolution of hydrogen chloride.

Germanium Tetrafluoride, GeF$_4$.—Germanium oxide dissolves in hydrofluoric acid, and the solution yields on evaporation over sulphuric acid crystals of GeF$_4$ + 3H$_2$O. When the vapors from a heated mixture of calcium fluoride and an excess of germanium oxide and sulphuric acid

are conducted into water, a strongly acid solution results, which is supposed to contain hydrogen germanium fluoride, H_2GeF_6.

Potassium Germanium Fluoride, K_2GeF_6, separates on mixing solutions of germanium fluoride and potassium fluoride. It is sparingly soluble in cold and more soluble in hot water.

Germanium Monoxide, GeO, results from the decomposition of the dichloride with potassium hydroxide.

Germanium Dioxide, GeO_2, is formed when the metal is burned in air, or is oxidized by nitric acid. It is best prepared by decomposing the tetrachloride with water and igniting the precipitate. It is somewhat soluble in water. Salts of the dioxide appear to exist, but have not been obtained of definite composition.

Germanium Monosulphide, GeS, is obtained by heating the disulphide for some time in hydrogen. Its observed gas density at 1100° is 51, theory requiring 52.

Germanium Disulphide, GS_2, separates as a white precipitate when a solution of the dioxide in sulphuric acid is treated with hydrogen sulphide. It is soluble in 222 parts of water.

Tin (Stannum), Sn.

Atomic Weight, 118. *Density,* 7.3.

Tin was an article of commerce before the Christian era. It is said to have been found native in small quantities. It occurs chiefly as dioxide, known as tin stone. There are but few tin mines, and the metal is not abundant. The tin stone is separated from the gangue by mechanical and chemical processes, and is reduced by heating with coal. The metal is purified, if necessary, by liquation. In this process the crude tin is gradually heated in a furnace, the pure tin flows off first, leaving less fusible alloys of tin. Commercial tin is liable to contain lead, copper, iron, zinc, antimony, and arsenic. Tin from Banca is fairly pure, containing only traces of impurities.

Tin is almost as white as silver, and is harder than lead, and somewhat softer than gold. It has a crystalline structure,

which causes the crackling or "tin cry" when a bar of the metal is bent. It is very malleable. At 100° it may be drawn into wire, but at 200° it is so brittle that it may be pulverized. At low temperatures (−40°) tin slowly becomes granular, and falls to a powder. It melts at 230°, undergoing slight oxidation in air, and at higher temperatures it burns to dioxide. At ordinary temperatures the lustre of tin is but little impaired by exposure to air and water. Tin dissolves in hydrochloric and dilute nitric acid, and is attacked by hot concentrated solutions of potassium and sodium hydroxides.

Since tin does not tarnish in air, and is not corroded by vinegar or other liquids used in cookery, the metal is especially valuable for culinary vessels. It is not sufficiently rigid for ordinary articles unless these are made quite heavy, and is, moreover, rather costly. Hence the metal is largely used as a protecting coating for iron and copper. The process of tinning sheet copper is as follows. The surface of the copper is carefully cleaned, wet with hydrochloric acid, to prevent formation of any oxide, and then molten tin is poured over the sheet, the excess of the tin being wiped off with cotton waste. Sheet iron is tinned by immersion in a bath of molten tin. After removal from the bath it is placed in hot tallow, so that the excess of tin may flow off. In order that the tin may adhere to the iron the latter must be carefully cleaned and protected from the air by a coating of tallow.

In place of pure tin an alloy of tin and lead, which is less costly, is largely used for tinning iron and copper. Such a coating has a bluish-leaden lustre. It answers for some purposes, but is quickly corroded by ordinary water, and is totally unfit for culinary vessels on account of the lead.

Tin may be deposited by electrolysis. When only a thin coating of tin is desired, brass and copper articles are tinned by immersion in a solution of the metal in which pieces of metallic tin are placed. Mirrors are coated with an amalgam of tin.

Tin is used in the form of foil for various purposes, but most of the so-called tin foil is chiefly lead between two surfaces of tin, and is made by rolling out plates of lead coated with tin.

Tin forms two classes of compounds, viz., the stannous, containing bivalent tin ; and the stannic, in which tin is tetravalent. Stannous tin is always basic, but stannic tin is acidic or basic according as it is combined with basic or acidic radicals.

Stannous Compounds.

Stannous Chloride, Tin Dichloride, $SnCl_2$ or $Sn{<}{Cl \atop Cl}$, is obtained by heating tin in dry hydrogen chloride or with mercuric chloride. Its gas density at 900° corresponds to that of molecules of $SnCl_2$. Tin dissolves in hydrochloric acid, and the solution on evaporating and cooling deposits crystals of the hydrate $SnCl_2 + 2H_2O$, known as tin salt. It dissolves in 0.37 part of water, but is decomposed by a large quantity of water with formation of a basic salt having the composition $2SnOHCl + H_2O$. This basic salt is insoluble in water, but soluble in hydrochloric acid. Tin salt, both in the dry state and in solution, absorbs oxygen from the air with formation of a white insoluble oxychloride. Stannous chloride is a strong reducing agent, separating metallic gold from a solution of gold chloride, and reducing cupric chloride to cuprous chloride. In these reactions stannous chloride is changed to stannic chloride. Tin salt is extensively used as a mordant in dyeing.

Stannous Oxide, SnO or $Sn{=}O$.—Potassium carbonate produces in a solution of stannous chloride a white precipitate of stannous oxyhydroxide, ${Sn \atop Sn}{<}{OH \atop O}{>}{\atop OH}$. This when heated in carbon

dioxide is converted into stannous oxide. The oxide takes fire when touched with a glowing splinter, and burns brilliantly, stannic oxide being formed.

Stannous Sulphide, SnS, results when tin foil burns in sulphur vapor. It forms a green vapor at high temperatures. Hydrogen sulphide throws down from stannous solutions a dark-brown precipitate of hydrous stannous sulphide.

Stannous Nitrate is obtained by dissolving tin in cold dilute nitric acid, part of the acid at the same time being reduced to ammonia :

$$4Sn + 10NO_2 - OH = 4{NO_2-O \atop NO_2-O} > Sn + NO_2-O-NH_4 + 3H_2O.$$
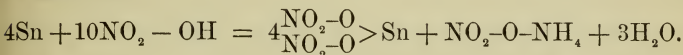
A solution of stannous nitrate decomposes on heating with separation of stannic hydroxide.

Stannous Sulphate, SnSO$_4$ or SO$_2 <{O \atop O}>$ Sn.—This salt is formed when concentrated sulphuric acid is heated with an excess of tin. Stannous sulphate is readily soluble in water, but the solution on standing deposits a basic salt.

Stannic Compounds.
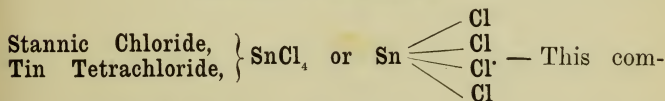
Stannic Chloride,
Tin Tetrachloride, } **SnCl$_4$ or Sn** $<{Cl \atop Cl} {Cl \atop Cl}$ — This compound is obtained by passing dry chlorine into molten tin in a retort; the vapor of the chloride is condensed in a cooled receiver. Stannic chloride is a colorless mobile liquid, boiling at 120°, and having a gas density corresponding to the formula SnCl$_4$. Exposed to moist air it takes up three molecules of water, and when its aqueous solution is evaporated at a moderate temperature crystals of the compound SnCl$_4$+5H$_2$O are deposited. A solution of stannic chloride, much used in

dyeing, is prepared by dissolving tin in aqua regia, kept cool
to avoid the formation of metastannic acid. Dilute aqueous
solutions of stannic chloride decompose on standing or when
warmed, with separation of stannic hydroxide. Stannic
chloride absorbs ammonia with formation of the compound
$SnCl_4.2NH_3$. This is dissociated by heat into stannic chloride
and ammonia gases, which recombine on cooling.

Hydrogen Stannic Chloride or Chlorostannic Acid, H_2SnCl_6.
—This compound is prepared by dissolving tin tetrachloride
in the required amount of concentrated hydrochloric acid, and
then passing in hydrochloric acid gas as long as it is absorbed.
On cooling, crystals separate having the composition H_2SnCl_6
$+ 6H_2O$. The ammonium and other salts of this acid have
long been known, but the acid has only recently been iso-
lated.

Ammonium Stannic Chloride, $(NH_4)_2SnCl_6$, is prepared by
mixing concentrated solutions of ammonium chloride and
stannic chloride, when a white crystalline meal separates.
The salt crystallizes in octahedrons, is permanent in air, and
is not decomposed in concentrated solution by boiling. A
dilute solution deposits stannic hydroxide on heating. This
change renders the salt valuable in dyeing, since the separated
hydroxide acts as a mordant.

Stannic Oxide, Tin Dioxide, SnO_2 or $O=Sn=O$, occurs
native as cassiterite or tin stone. It is formed artificially by
heating tin in air or by igniting stannic hydroxide. The
amorphous stannic oxide thus obtained may be changed into
microscopic crystals of the same form as cassiterite by heating
in hydrochloric acid gas. Stannic oxide is fusible only at
a very high temperature, and is insoluble in acids, excepting
concentrated sulphuric acid, with which it forms a syrupy
liquid, the dioxide separating again on dilution with water.
Stannic oxide is rendered soluble by fusion with potassium or

sodium hydroxide, and with a mixture of sodium carbonate and sulphur. It is easily reduced to the metal when heated in contact with charcoal or reducing gases. It is used in the manufacture of opaque white glass.

Stannic Hydroxides exist in two modifications, known as stannic and metastannic acids, differing in their behavior towards solvents, and forming two classes of salts.

Stannic Acid is formed as a white precipitate when a solution of stannic chloride is treated with calcium carbonate not in excess, and is also obtained when an acid is carefully added to a solution of a stannate. It is slightly soluble in water, and reacts acid. Dried over sulphuric acid it has the composition H_2SnO_3. It dissolves easily in hydrochloric, nitric, and sulphuric acids, and in solutions of the caustic alkalies.

Potassium Stannate, K_2SnO_3, is formed when stannic oxide is fused with potassium hydroxide. It is readily soluble in water, and crystallizes as $K_2SnO_3 + 3H_2O$.

Sodium Stannate, Na_2SnO_3, is prepared in the same way as the corresponding potassium salt, and also by heating tin with sodium hydroxide and sodium nitrate. The solution yields crystals of $Na_2SnO_3 + 3H_2O$. The salt is used in calico printing. The alkali stannates are the only soluble stannates, and from their solutions metallic stannates are precipitated on the addition of solutions of metallic salts.

Metastannic Acid.—Tin and concentrated nitric acid react violently with formation of a white insoluble powder, which after drying at 100° has the composition H_2SnO_3. The salts of metastannic acid indicate that it has the formula $H_{10}Sn_5O_{15}$. Metastannic acid dissolves slowly in solutions of potassium and sodium hydroxide with formation of potassium and sodium metastannates.

Sodium Metastannate, $Na_2H_8Sn_5O_{15}$, is a slightly soluble crystalline powder obtained by treating metastannic acid with a cold solution of sodium hydroxide.

Stannic Sulphide, SnS_2, is not formed by the direct union of its elements. It may be obtained by heating a mixture of tin amalgam, sulphur, and ammonium chloride in a retort. Part of the stannic sulphide will remain in the bottom of the retort, and part will sublime in golden-yellow crystals. The crystalline stannic sulphide is used as a pigment under the name of mosaic gold. Hydrogen sulphide in excess produces in solutions of stannic chloride a yellow precipitate of stannic sulphide which is soluble in alkali sulphides, with formation of sulphostannates. The compounds $Na_2SnS_3 + H_2O$ and $Na_4SnS_4 + 12H_2O$ have been prepared. The former yields, on treatment with hydrochloric acid, sulphostannic acid, H_2SnS_3.

Exp. 226.—Granulate tin by pouring the molten metal in a thin stream into water.

Exp. 227.—Moisten a clean sheet of copper with hydrochloric acid, then melt a bit of tin on the copper, and rub the tin over the copper with a rag moistened with acid.

Exp 228.—*a.* Digest pure tin foil or granulated tin with concentrated hydrochloric acid for some time. To half of the solution add potassium chlorate until chlorine is evolved. Expel the free chlorine by heating the solution. The potassium chlorate will convert the stannous into stannic chloride, the chlorate being reduced to chloride.

b. Try the reaction of hydrogen sulphide with dilute solutions of stannous chloride, and of stannic chloride. Dissolve the moderately washed precipitate of stannous sulphide in the least possible quantity of yellow ammonium sulphide. The solution when acidified with hydrochloric acid will give a yellow precipitate, showing that the tin had changed from the stannous to the stannic state.

Exp. 229.—Treat tin with concentrated nitric acid. What compound of tin is formed?

Lead (Plumbum), Pb.

Atomic Weight, 207.   *Density*, 11.35.

Metallic lead occurs very sparingly in nature, but its compounds are abundant and widely distributed. The most important ore of lead is galena, PbS. The smelting of galena when free from sulphides of other metals is very simple. The ore is roasted in a suitable furnace until the sulphur is burned away and lead remains. At first a portion of the lead sulphide is converted by the oxygen of the air into lead oxide and sulphate. The heat is then raised and the oxide and sulphate react with undecomposed sulphide to form sulphur dioxide, which passes off, leaving metallic lead:

$$2PbO + PbS = 3Pb + SO_2;$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$
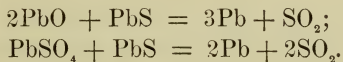
Lead has a light bluish-gray color, and the fresh-cut surface shows high lustre, which is soon dimmed by superficial oxidation. It is soft, easily scratched and cut, and leaves a bluish mark on paper. It ranks sixth among metals in malleability, and eighth in ductility. It has little tensile strength, a wire $\frac{1}{12}$ of an inch in diameter breaking with a load of 20 pounds. It melts at 334°, and volatilizes between 1400° and 1600°. On solidifying it contracts to such a degree that it is poorly adapted for making castings. Molten lead oxidizes in the air, and when the temperature is sufficient to melt the oxide, the latter is absorbed to a slight extent by the lead, rendering the metal harder. The lead of commerce is sometimes very pure, containing only slight traces of copper, iron, and silver. It is also liable to contain antimony, zinc, nickel, and bismuth.

Lead is only slightly attacked by hydrochloric acid and dilute sulphuric acid, but is dissolved by warm concentrated sulphuric acid. The best solvent for lead is moderately strong

hot nitric acid.   Soluble lead salts are poisonous, and when taken continuously into the system, even in small quantities produce nervous prostration, paralysis, and other disorders. Large doses of the soluble salts, as lead acetate, produce acute poisoning, and may cause death in a few days.   Metallic lead is not poisonous to handle, and hence plumbers are not subject to lead poisoning.

The action of drinking waters upon lead is of interest, since water which passes through lead pipes may be contaminated with lead.

Lead is not corroded by dry air nor by water free from air, while in water containing air it tarnishes quickly.   If the water is soft, such as rain water or ordinary distilled water, a white coating of lead hydroxide is rapidly formed, which is converted into a basic carbonate by the carbon dioxide absorbed from the air.   The white compounds formed by the combined action of air and water on lead do not adhere to the metal, but scale off, thus exposing fresh surfaces and allowing the corrosion to continue.   When the surface of lead is large in proportion to the bulk of water the latter soon becomes milky white from the suspended particles of lead carbonate and hydroxide, only a small quantity of the latter being dissolved by the water.

Drinking waters, rain water excepted, often contain salts which have a marked influence on the corrosion of lead. Ammonium nitrate, which is one of the products of the decomposition of organic matter in water, increases the action on the lead, while other nitrates appear to have little effect. Hard water is less liable to take up lead than soft water, owing to formation of an insoluble and coherent scale by the sulphates and carbonates of hard water, the scale preventing further corrosion.   As a rule, water which has stood in lead pipes or in lead or pewter vessels is unfit for drinking, but water is not contaminated by passing rapidly through a lead pipe.

Exp. 230.—*a.* Place a bright strip of lead in a bottle of distilled water. *b.* Place another piece of lead in the drinking water at hand. Allow the bottles to stand for some time, best loosely stoppered. The corrosion of the lead in the distilled water will continue for years if preparation *a* is kept, while the action of the drinking water will depend upon the impurities it contains.

Alloys of Lead and Tin.—These metals mix on fusion in all proportions. The following table gives the composition and melting points of some of the alloys:

				Melting Point.
Tin,	. . . . .			230°
		Lead,	.	334°
No. 1, ...	1	2		226°
" 2, ...	1	1		188°
" 3, ...	2	1		170°
" 4, ...	3	1		178°

The solder used for soldering tinware and joining lead pipes in plumbing varies much in composition. No. 1 is coarse, 2 is common, and 3 is fine solder. Solder is not only more fusible than either of the metals, but is much harder and stronger.

Lead in most of its combinations is bivalent, its tetravalent character only appearing in lead methyl, $Pb(CH_3)_4$, lead ethyl, $Pb(C_2H_5)_4$, and a few other compounds.

Lead Chloride, $PbCl_2$, or $Pb{<}^{Cl}_{Cl}$, is obtained by treating lead oxide, carbonate, or sulphide with hydrochloric acid, and also as a white crystalline precipitate on addition of a soluble chloride to a solution of a lead salt. It is soluble in 135 parts of water at 122°.5, and in less than 30 parts of boiling water. Lead chloride boils between 860° and 1000°. Its observed gas density is 140; theory requiring 139 for $PbCl_2$.

Lead chloride and oxide combine to form several oxychlorides. The hydroxychloride, $PbOHCl$, obtained by treating lead chloride with lime water, is used as a white pigment.

On passing chlorine into a mixture of concentrated hydrochloric acid and lead chloride a red solution is obtained, from which lead dioxide separates on addition of water. Lead dioxide forms with concentrated hydrochloric acid a similar red solution. These reactions indicate the formation of lead tetrachloride, $PbCl_4$.

Lead Iodide, PbI_2, separates as a yellow precipitate when a soluble iodide is added to a solution of a lead salt. From hot solutions it crystallizes on cooling in golden leaflets.

Lead Suboxide, Pb_2O, is obtained as a black powder by heating lead oxalate out of contact with oxygen:

$$2 \begin{matrix} COO \\ | \\ COO \end{matrix} \Big\rangle Pb = Pb_2O + 3CO_2 + CO.$$
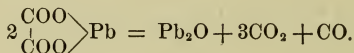
It is decomposed at a dull red heat into lead and lead oxide. Acids effect the same decomposition, the oxide reacting with the acids to form salts.

Lead Oxide, PbO or Pb=O, is formed when lead is heated in air, the metal being first coated with the suboxide, which is soon converted into the oxide. If the lead is constantly stirred and the temperature kept below the melting point of the oxide a gray ash is formed, consisting of oxide mixed with finely divided metallic lead, which is completely converted into oxide by continued heating. The oxide thus prepared, and known as massicot, has a bright yellow color. If lead is heated in air to a temperature at which the oxide fuses, the latter flows from the surface of the metal as fast as formed. The molten oxide solidifies to a yellowish or reddish mass of soft scales which is known as litharge. It is obtained in large quantities in cupellation of silver lead alloys. It is used in the manufacture of lead salts, in the preparation of drying oils, and for a cheap glaze on earthenware.

Lead oxide absorbs carbon dioxide (11 per cent has been found) and moisture from the air. It is soluble in a solu-

tion of potassium hydroxide, and from the hot concentrated solution yellow rhombic crystals of the oxide separate on cooling. Red tetragonal crystals are obtained when a molten mixture of lead oxide and potassium hydroxide is slowly cooled.

Lead Oxyhydroxide, HO–Pb–O–Pb–OH, is obtained as a white precipitate when an alkali hydroxide is added to a solution of lead acetate. If ammonia is used, the compound $3PbO.H_2O$ is said to be formed. Lead oxyhydroxide is soluble in alkali hydroxides, and to a slight extent in water. The aqueous solution absorbs carbon dioxide from the air, and becomes turbid.

Red Lead or Minium.—When lead oxide is carefully heated in air it takes up from 1.5 to 2.5 per cent of oxygen, and the color changes to a bright red. The product may be regarded as a mixture of compounds of lead oxide and dioxide. Red lead is largely used as a pigment, and in the manufacture of glass. It is converted by ignition into oxide.

Lead Dioxide, PbO_2, is obtained as a brown powder by digesting red lead with dilute nitric acid. It is manufactured on a large scale by cheaper methods.

Exp. 231.—Add red lead gradually, and with constant stirring, to nitric acid diluted with its bulk of water. Collect the oxide on a filter, wash and dry it. Lead nitrate may be obtained in crystals by evaporating the acid filtrate.

Lead dioxide loses half its oxygen on heating, and acts as a powerful oxidizing agent towards combustible matter. It has feeble basic peoperties, and forms the salt $PbO(C_2H_3O_2)_2$, which is soluble in glacial acetic acid, and is decomposed by water into PbO_2 and acetic acid. Lead dioxide dissolves in very concentrated potassium hydroxide, and the solution yields on evaporation in vacuum hydrous crystals of potas-

sium plumbate, $O=Pb\begin{subarray}{l}O-K\\O-K\end{subarray} + 3H_2O$. This compound is analogous to carbonates.

Lead Sulphide, PbS, occurs as galena, crystallized in cubes or modifications of cubes of a bluish-gray color. Hydrogen sulphide precipitates from solutions of lead the sulphide as an amorphous black mass. In presence of hydrochloric acid a reddish precipitate of lead chlorosulphide is sometimes formed, which is converted into lead sulphide by an excess of hydrogen sulphide. Lead sulphide dissolves in concentrated hydrochloric acid, hydrogen sulphide being evolved. Nitric acid converts it into lead nitrate and sulphate.

Lead Acetate, $Pb(C_2H_3O_2)_2$ or $\begin{subarray}{l}CH_3COO\\CH_3COO\end{subarray}>Pb$.—This salt is manufactured in large quantities by dissolving lead oxide in acetic acid. It is soluble in 1.5 parts of water at ordinary temperature and 0.5 part above 100°. The hot solution deposits on cooling crystals containing 3 molecules of water. Solutions of lead acetate dissolve lead oxide, with formation of basic acetates. Solutions of these basic compounds rapidly absorb carbon dioxide from the air, and become turbid from separation of lead carbonate. Lead acetate has a slightly sweetish taste, and is commonly known as sugar of lead. It is used extensively in the arts, in the preparation of lead chromate, and other pigments.

Lead Nitrate, $Pb(NO_3)_2$ or $\begin{subarray}{l}NO_2-O\\NO_2-O\end{subarray}>Pb$.—This salt, made by dissolving lead oxide in dilute nitric acid, is very soluble in water, but insoluble in strong nitric acid.

Lead Sulphate, $PbSO_4$ or $SO_2<\begin{subarray}{l}O\\O\end{subarray}>Pb$.—This salt separates as a heavy white powder when sulphuric acid or a soluble sulphate is added to a solution of a lead salt. It is soluble in

22,816 parts of water, and in 36,500 parts of dilute sulphuric acid. It is more soluble in the concentrated acid, but separates on diluting the acid solution with water. Lead sulphate is somewhat soluble in dilute nitric acid, and readily soluble in ammonium acetate.

Lead Carbonate, $PbCO_3$, occurs as the mineral cerusite in crystals isomorphous with arragonite. It is obtained artificially by pouring a solution of lead nitrate into ammonium carbonate. The precipitate produced by sodium carbonate in solutions of lead salts is a basic carbonate of variable composition.

White Lead.—This substance is a mixture of basic carbonates which may be viewed as lead carbonate with varying proportions of lead hydroxide. It yields on ignition from 85 to 86.3 per cent of lead oxide. White lead forms with a drying oil an opaque white mixture, which is remarkable for its covering power, and is the best basis for paints. White lead is largely adulterated with barytes (barium sulphate).

There are several processes employed in the manufacture of white lead, the Dutch process being the oldest. In this process sheets of lead in the form of a spiral are placed in earthen pots containing dilute acetic acid or vinegar. A number of pots are piled together and covered with horse manure or spent tan-bark. The vapor of acetic acid and the oxygen of the air attack the lead, a basic acetate being formed. The fermentation of the bark or manure supplies carbon dioxide, which converts the basic acetate into basic carbonate. The acetic acid set free converts a further portion of lead into acetate, which in turn is decomposed, and hence but little acid is required in the process. After some weeks the white lead is detached from the metallic lead remaining, and ground while moist to a paste, washed to remove acetic acid, and then dried.

In the French process a solution of basic lead acetate is prepared by digesting litharge with a solution of lead acetate. Carbon dioxide is then passed into the solution. The basic acetate is decomposed, with separation of white lead, which is allowed to settle. The supernatant liquor, containing lead acetate and free acetic acid, is drawn off and treated with litharge for a new solution of basic acetate. The white lead is washed by decantation and dried.

———————

The student may easily prepare the lead salts of hydrochloric, nitric, and sulphuric acids, and may verify by experiments some of the statements made about these salts, and also about the oxides and the sulphide of lead. He should formulate the reactions involved in the experiments.

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Summary of the Fourth Group.

	Atomic Weight.	Density.	Fusing Point.
Carbon,	12	3.5	Infusible.
Silicon,	28	2.5	White heat.
Titanium,	48	—	———
Zirconium,	90.7	4.1	Infusible.
Cerium,	141	6.6	Below 1000°.
Thorium,	232	11	Infusible.
Germanium,	72	5.5	900°.
Tin,	118	7.3	230°.
Lead,	207	11.35	334°.

The densities of the elements of this group increase with the atomic weights from carbon and silicon to thorium, and from germanium to lead. Most of them are infusible, or fusible only at very high temperatures. Tin and lead, however, are readily fusible. While the members of the group present few analogies in physical properties, they exhibit to a

striking degree in their compounds a similarity in chemical characteristics. With the halogens all the members of the group except cerium form tetrahalides, and all form dioxides. Carbon is acidic in carbonates, but with hydrogen it forms basic radicals. Silicon is acidic, while titanium with the next higher atomic weight is both acidic and basic. Zirconium has more pronounced basic characters, and cerium and thorium exhibit only basic properties.

Tin forms acid hydroxides, and the salts which the metal forms with oxygen acids have little stability. Lead, on the contrary, is strongly basic, and forms well-defined salts containing bivalent lead.

Cerium forms by preference compounds analogous to those of the third group, as for example, $CeCl_3$ and $Ce_2(SO_4)_3$.

The student should make a table of the formulas of the compounds of the group which have been described, placing analogous compounds in the same column. Such a table will exhibit the chemical analogies existing between the different members of the group.

THE EIGHTH GROUP.

The members of this group are iron, cobalt, and nickel, and the platinum metals, which are ruthenium, rhodium, palladium, platinum, iridium, and osmium. The platinum metals are so called because of their similarity to platinum, with which they are associated in nature, all occurring in the metallic state.

Iron (Ferrum), Fe.

Atomic Weight, 56. *Density,* 7.84.

Iron is the most useful of metals. No other metal possesses such a variety of valuable properties, or can be used instead of it for cutting-tools. Iron is widely distributed, occurring in all soils and most rocks, and is a constituent of many minerals. It is found in small quantities in animals and plants, and in many natural waters. The minerals limonite, $2Fe_2O_3 + 3H_2O$, and oxides of iron with less water, also hematite, Fe_2O_3, magnetite, Fe_3O_4, and siderite, $FeCO_3$, constitute the ores of iron. Some of the ores are nearly pure, but most of them are mixed with earthy matter, limestone, quartz, and compounds of manganese. Sulphur and phosphorus are usually found in small quantities in the ores, and are troublesome impurities, owing to difficulty in separating them from the iron.

The different kinds of iron used in the arts are comprised under three heads, viz.: Wrought Iron, Steel, and Cast Iron. Their differences are exhibited in part by the following table:

Chemical Composition.	WROUGHT IRON.	STEEL.	CAST IRON.
Carbon	traces to 0.4	0.4 to 1.8	2 to 5
Silicon	0 to 0.2	0 to 0.4	0.1 to 3
Sulphur	0 to 0.1	0 to 0.1	traces to 0 5
Phosphorus	0 to 0.5	0 to 0.3	traces to 2
Manganese	traces	traces	traces to 2 and more
Iron	99 to 99.5	97 to 99.5	90 to 97
Essential Composition.	Nearly pure iron, with little impurity besides carbon.	Iron containing 0.4 to 1.8 per cent. of carbon. Bessemer steel sometimes contains 2 per cent or more of manganese.	Impure iron, containing 2 to 5 per cent. of carbon, with variable amounts of silicon, sulphur, phosphorus, and manganese.
Physical Characteristics.	Welds readily; is not as hard as steel; very difficultly fusible; does not harden when quickly cooled; texture fibrous; very tough and tenacious when of good quality. Slight hardening is first noticeable when the amount of carbon is about 0.35 per cent.	Welds, but with greater difficulty with increase of carbon; more fusible than wrought iron, the fusing point being lower the higher the content of carbon; can be hardened by sudden cooling; can be annealed; will bear a cutting edge; when of good quality is tough, and much more elastic than wrought iron; texture fine, granular, or slightly fibrous, according to mode of preparation.	Will not weld; is more fusible than steel, and is readily cast; will not harden like steel; much more brittle than steel or wrought iron, but possessing considerable strength, especially as regards crushing strain; texture crystalline or granular.

Manufacture of Cast Iron.—Most of the iron of commerce is obtained by the reduction of ores to cast or pig iron in blast furnaces. These furnaces vary greatly in size and shape, but are essentially shafts narrowed at the top and bottom, and having a height of 30 to 90 feet. Their capacity varies from 4000 to 40,000 cubic feet. The furnace is charged at the top with ore and fuel, the latter being either hard coal, coke, or charcoal. Limestone is usually added as a flux to form a fusible slag with the impurities of the ore. A blast of air is blown through four or more openings called tuyères, near the bottom of the furnace. The oxygen of the air and the incandescent carbon form carbon monoxide, which passes upwards, and near the top of the furnace reduces the lumps of the ore to porous masses of unfused iron. The carbon monoxide takes the oxygen from the oxide of iron, carbon dioxide being formed. As the iron sinks in the furnace it is exposed to higher temperatures, and very complicated reactions occur between the iron and the oxides of carbon, and perhaps other gases, and the fuel. At this stage of the process the iron takes up carbon and silicon, and is converted into cast iron, which fuses and sinks to the bottom of the furnace. The impurities of the ore unite with the flux to form a liquid slag, which floats on top of the liquid iron, and flows from an opening in the side of the furnace. The iron is drawn off from time to time, and cast into pigs.

Varieties of Cast Iron.—The kind of iron made in a blast furnace depends upon the quality of the ore, and partly upon the amount of fuel and blast used. Gray irons contain carbon, partly in combination with iron, and partly as graphite mechanically mixed. In white iron nearly all the carbon is in combination. Intermediate between these two kinds are the mottled irons. Gray iron is used for ordinary castings. Spiegeleisen is a variety of white iron which is very hard and brittle, containing considerable manganese, and more carbon

than other varieties of iron. Certain qualities of gray iron when suddenly cooled from the molten state are converted into white iron, and are said to chill. Chilled iron is harder and resists wear better, but is more brittle, than ordinary gray iron. Cast-iron car-wheels are made of a good quality of iron, cast in a mould with a band of iron to chill the rim of the wheel to a depth of about an inch; the remainder of the wheel, cooling slowly in the sand, is tough gray iron.

Manufacture of Wrought Iron.—The ores of iron are reduced by heating in a suitable fire or furnace to a sponge-like mass of wrought iron. This method, which is costly in fuel, and does not admit of production on a large scale, was probably the earliest method, and is still employed by natives of India and Central Africa. Wrought iron is commonly made by burning out the carbon, silicon, sulphur, and phosphorus of cast iron by the puddling process. In this process pig iron is melted by an oxidizing flame on the hearth of a furnace, and stirred or puddled in order to expose fresh surfaces of the molten metal to the action of oxygen, some iron oxide being added to facilitate the oxidation of the impurities. The iron gradually becomes less fusible, and at last changes to a pasty mass. It is then gathered into lumps, which are removed from the furnace, and squeezed and hammered to get rid of slag, and finally rolled into bars. The iron is made more homogeneous and tougher by heating bundles of bars to a welding heat and rolling again.

Manufacture of Steel.—It is not found practicable to make steel directly from pig iron by burning out only part of the carbon. In the manufacture of steel by the cementation process bars of wrought iron are heated for some days in contact with charcoal powder. The iron slowly takes up carbon and changes to steel. The metal is not uniform in composition or structure, and to overcome these imperfections it is

melted in crucibles and cast into ingots. The product at this stage is coarsely crystalline, and contains cavities. The ingots are heated and rolled, and the steel is thus rendered fine-grained and tougher. The finest qualities of tool steel are made by the cementation process.

The Bessemer method of making steel is much less costly than the one just described. In this process molten cast iron is run into a large vessel called a converter, which is lined with an infusible mixture of clay and quartz, and a powerful blast of air is blown into the molten metal through a number of small holes in the bottom of the converter. The silicon, carbon, and other impurities burn out rapidly, leaving nearly pure iron. Spiegeleisen is then added in order to introduce the requisite amount of carbon, and the metal is poured from the converter into moulds. The ingots of steel thus produced are afterwards rolled while hot.

The Bessemer process is well adapted for making low steels, i.e., steels with little carbon, which have largely replaced wrought iron for railroad rails, boiler-plates, and other purposes. Formerly all varieties of Bessemer metal were called steel, but at the present time if the carbon content is so low that the metal will not harden it is called ingot iron.

In the so-called "basic process" the converter has a lining chiefly of lime. In the older processes a portion of the phosphorus in the cast iron remains in the steel, whereas in the basic process the phosphorus is removed by the lime.

There are other methods of making steel, such as melting together wrought and cast iron in crucibles, and by smelting ores on a hearth and then adding spiegeleisen.

Preparation of Pure Iron.—Pure iron is little known. It has been obtained by various methods, one of which is the following. Pure iron oxide is reduced by hydrogen in a platinum crucible, and the finely divided iron thus obtained is then fused in a lime crucible by means of an oxyhydrogen blow-pipe supplied with pure gases.

Properties of Iron and Steel.—These have been given in part in the table on page 395. Pure iron is almost silver white, and possesses greater tensile strength than any other metal, excepting nickel and cobalt. It is softer, tougher, and has a higher melting point than ordinary wrought iron, which it resembles in other properties.

Wrought iron possesses the valuable property of softening at a red heat, when it can be forged or rolled into any desired shape. At higher temperatures it welds; that is, pieces with clean surfaces adhere and form a homogeneous mass when hammered together. Steel does not weld readily, but steel and wrought iron are easily welded together.

The tensile strength of puddled iron varies from 20 to 30 tons per square inch; ingot Bessemer iron from 30 to 40 tons; steel is stronger, and steel wire has been made with a breaking strain of 92 tons per square inch of cross-section.

Sulphur, other than in minute traces, renders iron and steel brittle when hot (red short), and phosphorus brittle when cold (cold short). These effects are modified to some extent by manganese, carbon, and silicon. A steel with 0.5 per cent of carbon and 0.1 per cent of sulphur is liable to be red short, and 0.1 per cent of phosphorus makes it cold short. Even 0.03 per cent of phosphorus injures tool steel.

Steel which has been heated to faint redness, and cooled by plunging into water, is very hard, and too brittle for use. To make it tougher the temper is drawn by heating, the progress of the change being judged from the tints on the polished surface due to oxidation. At about 230° the steel becomes a light straw yellow, and is still very hard; at 243° the color is full yellow, and the temper is suitable for razors; at 255° a brownish yellow appears, and the temper is adapted to cold chisels; at 265° purple first appears, and the temper is suitable for axes; at 288° bright blue is seen, which is the color for watch-springs; at higher temperatures up to 316° softer tempers result. Steel and iron are annealed by slow cooling.

Iron does not change in dry air, nor in water free from air, but when exposed to common air or water it rusts, and the rusting is hastened by the presence of acids, even carbonic. Lime water and other alkaline solutions prevent the rusting of iron. A highly polished surface resists corrosion longer than a rough surface. Any covering, such as paint, oil, or graphite, prevents rusting. A very effective protection is obtained by heating iron and steel articles in air, carbon dioxide, or steam, until a coating of magnetic oxide is formed. The so-called "galvanized iron" is iron coated with zinc by immersion in a bath of molten zinc. The coating of zinc prevents the iron from rusting.

Iron when hot burns readily in air and oxygen, and also in sulphur vapor. It unites with the halogens at ordinary temperature. White cast iron is less readily soluble in acids than gray cast iron or wrought iron.

Iron forms two well-defined classes of compounds, viz., ferrous, in which Fe is apparently bivalent, as in $FeCl_2$; and ferric, in which Fe is assumed to be trivalent, as in $FeCl_3$. Iron is also regarded by chemists as tetravalent, and the constitution of the two series of salts has been expressed by such formulas as

$$\frac{Cl}{Cl}{>}Fe{=}Fe{<}\frac{Cl}{Cl}, \quad \text{and} \quad \frac{Cl}{Cl}{>}Fe{-}Fe{<}\frac{Cl}{Cl}.$$
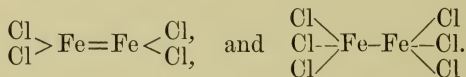
In this book the simpler formulas are used.

Ferrous Compounds.

Ferrous Chloride, $FeCl_2$ or $Fe{<}\frac{Cl}{Cl}$, is obtained in colorless scales when hydrochloric acid gas is passed over red-hot iron wire, and also by reducing ferric chloride in a current of hydrogen. It is very deliquescent, fuses at a red heat, and vola-

tilizes only at a high temperature. Its gas density has been found to be 92.5 at a yellow heat; $FeCl_2$ requires 63.2 and Fe_2Cl_4 126.4 : hence it appears that Fe_2Cl_4 exists, decomposing, however, at higher temperatures into $FeCl_2$. The hydrate, $FeCl_2 + 4H_2O$, is obtained in bluish crystals when a hot concentrated solution of iron in hydrochloric acid is cooled out of contact with air.

Ferrous Iodide, FeI_2 or $Fe < {}^I_I$, is formed by the direct union of its elements. A solution of the salt is easily prepared by digesting iron filings with iodine and water. The colorless or bluish-green solution absorbs oxygen from the air, and decomposes with separation of iodine and formation of ferric hydroxide. Ferrous iodide is used in medicine.

Ferrous Oxide, FeO or $Fe{=}O$.—This oxide is obtained by heating ferric oxide to 500° in a current of hydrogen. It is a black powder, which rapidly oxidizes in air.

Ferrous Hydroxide, $Fe(OH)_2$ or $Fe < {}^{OH}_{OH}$.—An alkali hydroxide produces in a solution of a pure ferrous salt a white flocculent precipitate of ferrous hydroxide. If the precipitate is washed out of contact with air and dried in hydrogen, the hydroxide remains in the form of a white powder. Ferrous hydroxide rapidly absorbs oxygen. It dissolves in about 150,000 parts of water, forming an alkaline solution having the taste of ferrous salts.

Ferrous Nitrate, $Fe(NO_3)_2$ or ${NO_2{-}O \atop NO_2{-}O} > Fe$.—This salt is obtained by dissolving ferrous sulphide in cold dilute nitric acid (density 1.12). The solution deposits on evaporation in vacuum at low temperatures crystals of $Fe(NO_3)_2 + 6H_2O$. A solution of ferrous nitrate, free from acid, may be boiled without decomposition, but in presence of free nitric acid it is con-

verted into ferric nitrate, and nitric oxide is given off. Iron dissolves in cold dilute nitric acid without evolution of hydrogen, and the solution contains ferrous nitrate and ammonium nitrate. Such a solution is used by dyers.

Ferrous Sulphate, FeSO$_4$ or SO$_2<{{O}\atop{O}}>$Fe.—A solution of this salt is obtained by dissolving iron in dilute sulphuric acid. On cooling a concentrated solution, and on evaporating a dilute solution, bluish-green monoclinic crystals of FeSO$_4$ + 7H$_2$O separate, which are known as green vitriol. Ferrous sulphate is very soluble, 100 parts of FeSO$_4$ + 7H$_2$O dissolving in 164 parts of water at 10° and 36 parts at 100°. Ferrous sulphate may be crystallized with five and with four molecules of water. The monohydrate, FeSO$_4$ + H$_2$O, is obtained as a white powder by heating green vitriol to 140° out of contact with air; at a little higher temperature the salt becomes anhydrous. Green vitriol, when pure and dry, does not absorb oxygen from the air unless the latter is very moist. The commercial salt commonly contains ferric sulphate, which changes the delicate bluish-green color of the pure salt to green. Crystals containing ferric sulphate become moist on exposure and slowly absorb oxygen, with formation of a reddish-yellow coating of basic ferric sulphate. Solutions of ferrous sulphate undergo the same change, and deposit a yellow basic ferric sulphate.

Green vitriol is manufactured in large quantities from iron pyrites, FeS$_2$, and it is a by-product in iron-works where iron is pickled or cleansed with sulphuric acid. It is used in dyeing, in purifying coal gas, and as a disinfectant.

Ferrous Ammonium Sulphate, FeSO$_4$.(NH$_4$)$_2$SO$_4$ + 6H$_2$O.— This salt separates in light bluish-green crystals on cooling a concentrated solution of green vitriol and ammonium sulphate, mixed in the requisite proportions. It is much more permanent than green vitriol, and on this account, and the

ease with which it is obtained pure, is useful in standardizing solutions required in the volumetric estimation of iron. It contains one seventh of its weight of iron.

Ferrous Carbonate, $FeCO_3$, occurs abundantly as an ore known as spathic iron. It is obtained artificially by heating to 150° for 12 to 36 hours a solution of ferrous sulphate to which sodium carbonate has been added. Thus prepared it is a white crystalline powder, which is not readily acted upon by acids, and is permanent in dry air. The hydrated ferrous carbonate separates on addition of an alkali carbonate to a ferrous solution as a white flocculent precipitate, which absorbs oxygen rapidly, gives off carbon dioxide, and finally changes to ferric hydroxide. If the precipitate is thoroughly washed with deaërated water, and dried in carbon dioxide, a greenish tasteless powder is obtained, which is tolerably permanent.

Ferrous carbonate and metallic iron dissolve to a slight extent in water containing carbon dioxide. Many natural waters contain iron held in solution by carbonic acid, and are known as chalybeate waters. The solution has a metallic flavor, and decomposes on exposure to air, with separation of ferric hydroxide. Solutions of ferrous carbonate have been recently used to purify sewage water.

Ferrous Sulphide, FeS.—This compound is made by dropping sulphur upon red-hot scrap iron. The iron and sulphur melt together, and on allowing the product to cool a brittle gray mass of ferrous sulphide is obtained. It is, however, liable to contain particles of uncombined iron. If sulphur is added to the hot sulphide, until the latter on cooling is yellow, owing to the formation of a higher sulphide, and the mass is then fused, a pure product is obtained. Ferrous sulphide is much used for the preparation of hydrogen sulphide. An amorphous hydrous ferrous sulphide is formed when ammonium sulphide is added to a ferrous solution. If a ferric salt

is used, the precipitate contains free sulphur. The reaction with ferric chloride is

$$2FeCl_3 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$
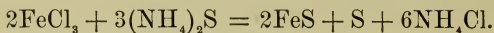
Hydrous ferrous sulphide absorbs oxygen rapidly on exposure to the air, and is converted into ferrous sulphate.

Iron Disulphide, FeS₂, is not a ferrous compound, but is conveniently noticed in connection with ferrous sulphide. It occurs as the mineral pyrite or pyrites in fine yellow crystals belonging to the cubic system. On heating FeS_2 half of the sulphur is given off, leaving ferrous sulphide. Pyrites is largely used for its sulphur in the manufacture of sulphuric acid.

Exp. 232.—*a.* Place in a flask 10 cc. of concentrated sulphuric acid, 30 cc. of water, and about 10 grams of fine iron wire. Warm gently, and after the reaction has nearly ceased filter the hot solution into a porcelain dish. On cooling, crystals (of what ?) will separate. Pour off the mother-liquor, and rinse the crystals once with a small quantity of water. *b.* Dry a portion of the crystals with filter paper. *c.* Leave another portion moist. *d.* Dissolve the remainder in water. Set all three preparations aside for a few days, and note any changes. Represent by an equation the reaction between the iron and acid, and state observations which support the view expressed by the equation.

Exp. 233.—Treat iron wire in a test-tube with dilute sulphuric acid. When considerable has dissolved pour the solution while boiling hot into a test-tube containing boiling dilute ammonia. The latter should be in excess. Formulate the reaction, and note color of precipitate and any changes it may undergo on standing.

Exp. 234.—Take 20 grams of green vitriol—the commercial article will answer—and the weight of common ammonium sulphate found by calculation to be required to form ferrous ammonium sulphate. Dissolve the two salts together in 50 cc. of boiling water, and filter the hot solution into a wide-mouthed bottle. Label and set aside. Crystals, often of considerable size, will separate after a day. Test some of the crystals for iron and for ammonia. Write equations of the reactions by which iron and ammonia are found.

Exp. 235.—Add ammonium sulphide to a solution of ferrous sulphate,

and wash the precipitate obtained on a filter several times with water. Leave a portion of the moist ferrous sulphide in a porcelain dish until next practice, when any changes may be noted. Treat another portion of the precipitate with dilute hydrochloric acid. What is the result?

Ferric Compounds.

Ferric Chloride, $FeCl_3$ or $Fe\begin{subarray}{l}\diagup Cl \\ - Cl \\ \diagdown Cl\end{subarray}$.—Hot iron burns in chlorine with the formation of this chloride. Chlorine converts ferrous chloride into the ferric salt. When a solution of ferric chloride is evaporated to dryness the dry residue consists of ferric chloride mixed with oxychloride, and on gentle ignition the former sublimes and condenses in the cooler parts of the apparatus. Ferric chloride forms grayish-black leaflets, very soluble in water and alcohol, and which deliquesce in air to a dark-red liquid.

The observed gas density of ferric chloride at 448° is 151.6; theory requires 162.2 for Fe_2Cl_6. At higher temperatures ferric chloride is partially dissociated into ferrous chloride and chlorine. It is possible that molecules of $FeCl_3$ and of Fe_2Cl_6 exist in the gaseous state.

A solution of ferric chloride is easily made by dissolving iron in hydrochloric acid, and then passing chlorine gas into the solution to convert the ferrous into ferric chloride; or by dissolving ferric oxide or hydroxide in hydrochloric acid. A concentrated solution of ferric chloride is brownish red, the color changing to a faint yellow on diluting the solution. The hydrate $FeCl_3 + 6H_2O$ is obtained as a solid crystalline mass when 100 parts of anhydrous ferric chloride are mixed with 63.5 parts of water.

Ferric Oxide, Fe_2O_3 or $O=Fe-O-Fe=O$, is also called sesquioxide of iron and red oxide of iron. It occurs as the mineral

hematite, which is one of the principal ores of iron. It is obtained artificially by igniting any of the ferric hydroxides or salts of iron with volatile acids. Ferric oxide of whatever source gives a red powder when pulverized. It is used in paint, and in the form of a powder called rouge is specially prepared for polishing glass. That used for polishing metals is called crocus. Strongly ignited ferric oxide dissolves slowly in hydrochloric and sulphuric acids.

Ferrous–Ferric Oxide, Magnetic Oxide of Iron, Fe_3O_4 or $O=Fe-O-Fe-O-Fe=O$.—This oxide occurs as magnetite, crystallized in octahedrons. It is widely distributed, and is the richest ore of iron, containing when pure 72 per cent of iron. It is easily distinguished by being strongly attracted by the magnet, and by yielding a black powder.

Some native magnetites, known as lodestones, possess the property of attracting iron and rendering it magnetic. The magnetite ores are not commonly lodestones, but often will lift small pieces of fine iron wire.

The magnetic scale formed when iron is heated in air is a varying mixture of ferrous and ferric oxide, the ferrous oxide predominating in the inner portion and the ferric oxide on the outside. Reference has already been made to the formation of magnetic oxide when hot iron and steel are exposed to steam or carbon dioxide. On the other hand, all the iron oxides are reduced to the metal by hydrogen and carbon monoxide at red heat.

When a solution of magnetic oxide in hydrochloric acid or a solution of ferrous and ferric salts in the right proportion is treated with ammonia, a black magnetic hydroxide is precipitated.

Ferric Hydroxides.—Ammonia produces in cold rather dilute solutions of ferric salts a bulky brownish-red precipitate of ferric hydroxide, $Fe(OH)_3$. This readily loses water, and

in boiling water becomes less bulky and darker colored. The dehydration may thus be carried so far that only 2 per cent of water will remain with the precipitate. Freshly precipitated ferric hydroxide dissolves readily in acid, but when more or less dehydrated dissolves slowly. Iron rust has the composition $Fe_2O_3 + 2Fe(OH)_3$.

Soluble Ferric Hydroxide.—Freshly precipitated ferric hydroxide dissolves in a solution of ferric chloride, forming a deep-red liquid. A similar solution is obtained when ammonium carbonate is added to ferric chloride until the precipitate formed no longer dissolves on shaking. If such a solution is dialyzed a red solution remains, which is nearly free from chlorides, and from which after some weeks gelatinous ferric hydroxide separates.

Ferric Nitrate, $Fe(NO_3)_3$ or $\begin{matrix} NO_2-O \\ NO_2-O \\ NO_2-O \end{matrix}\!\!\!\!\Big\rangle Fe$.—When iron dissolves in nitric acid, density 1.034, ferrous nitrate is formed, together with ammonium nitrate, as stated under ferrous nitrate. If, however, acid having a density of 1.115 is taken, only ferric nitrate is formed, and no ammonium salt. Crystalline hydrates of ferric nitrate have been obtained from concentrated solutions. When a solution of ferric nitrate is evaporated in a water-bath, nitric acid is given off, and a residue remains from which water dissolves little, and which is slowly taken up by hot nitric acid. Ferric nitrate is used in dyeing.

Ferric Sulphate, $Fe_2(SO_4)_3$ or $\begin{matrix} SO_2{<}^O_O{>}Fe \\ SO_2{<}^O_O \\ SO_2{<}^O_O{>}Fe \end{matrix}$.—This salt is easily prepared by adding sulphuric and nitric acids to a solution of ferrous sulphate :

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$
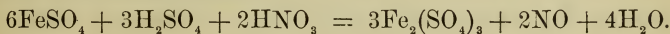
When a solution containing an excess of sulphuric acid is evaporated, the salt separates as a white powder, which dissolves with difficulty in water. The presence of a small quantity of ferrous sulphate facilitates the solution. A number of complex basic ferric sulphates have been described.

Ferric Ammonium Sulphate, $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 24H_2O$. — This double salt is an iron alum. It is made by adding the required amount of ammonium sulphate to a solution of ferric sulphate containing a little free sulphuric acid. The solution deposits on spontaneous evaporation octahedral crystals of the alum. It is employed in dyeing, when a perfectly neutral ferric salt is required.

Exp. 236.—To a solution of green vitriol add some sulphuric acid, then drop by drop nitric acid, until on warming red fumes are no longer evolved and the green solution has become reddish. Dilute a portion of the solution of ferric sulphate with water, and add ammonia in excess. Express the reaction by an equation. Boil for some time, and observe that the precipitate becomes denser and darker colored. Wash the precipitate thoroughly on a filter with hot water, dry at 100°, and, after removing from the filter, ignite in a porcelain crucible. The ferric oxide thus prepared will yield a red powder when rubbed in a mortar.

Ferric Acid, H_2FeO_4, is not known in the free state. When fine iron filings are fused with two parts of potassium nitrate, the mass after cooling yields with water a red solution, which contains potassium ferrate. The same salt is also formed when chlorine is passed through a solution of potassium hydroxide in which ferric hydroxide is suspended. Potassium ferrate is unstable, decomposing readily in aqueous solution, with separation of ferric hydroxide and evolution of oxygen. Alkaline solutions are more permanent. Barium ferrate, $BaFeO_4 + H_2O$, separates as a dark-red powder when barium chloride is added to a solution of the potassium salt.

Iron Cyanides.

Silver cyanide dissolves in a solution of potassium cyanide, forming the double salt $AgCN.KCN$. Nitric acid decom-

poses this compound, precipitating silver cyanide and setting free hydrocyanic acid, thus:

$$AgCN.KCN + HNO_3 = AgCN + HCN + KNO_3.$$
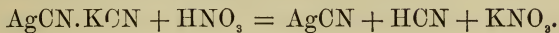
Hydrogen sulphide separates the silver from the cyanogen:

$$2(AgCN.KCN) + H_2S = Ag_2S + 2HCN + 2KCN.$$
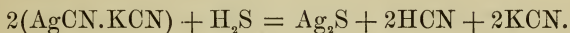
Potassium cyanide produces in solutions of zinc salts a white precipitate of zinc cyanide, which forms with potassium cyanide the soluble salt $2KCN.Zn(CN)_2$. This salt is decomposed by nitric acid, with separation of all of the cyanogen as hydrocyanic acid:

$$2KCN.Zn(CN)_2 + 4HNO_3 = 4HCN + 2KNO_3 + Zn(NO_3)_2.$$
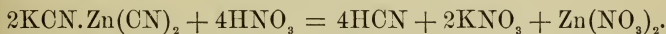
Ammonium sulphide precipitates the zinc as sulphide:

$$2KCN.Zn(CN)_2 + (NH_4)_2S = ZnS + 2KCN + 2NH_4CN.$$
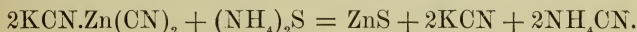
A number of double cyanides are decomposed with separation of cyanogen from the metals by reactions analogous to those above given. There are, however, compounds containing iron and cyanogen, known as ferro- and ferricyanides, which exhibit a different deportment. The iron and cyanogen in them are not separated from each other by reagents which precipitate iron from its ordinary salts, such as ferrous sulphate or ferric chloride, or which separate cyanogen from potassium, zinc, or silver cyanide.

Potassium cyanide produces in a solution of ferrous sulphate a yellowish-red precipitate, soluble in an excess of potassium cyanide, with formation of potassium ferrocyanide, $K_4(C_3N_3)_2Fe$. From solutions of this salt acids fail to separate ferrous cyanide, or at common temperature to set free hydrocyanic acid. Moreover, neither ammonium sulphide nor alkalies separate the iron from potassium ferrocyanide. The potassium in $K_4(C_3N_3)_2Fe$ can be replaced by hydrogen, and

by metals such as lead, calcium, and zinc, without, however, separating the iron from the cyanogen. These reactions show that iron and cyanogen are united in a compound radical, which can be transferred from one compound to another without losing its identity.

Assuming that the precipitate which potassium cyanide produces in a solution of ferrous sulphate is ferrous cyanide, a compound not yet obtained pure, we may represent the formation of potassium ferrocyanide thus:

$$Fe(CN)_2 + 4KCN = K_4(C_3N_3)_2Fe.$$

Tricyanogen chloride, $C_3N_3Cl_3$, is the acid chloride of cyanuric acid, $C_3N_3(OH)_3$, both compounds containing the trivalent radical tricyanogen, C_3N_3. Cyanuric acid is formed when anhydrous potassium ferrocyanide is heated with bromine, and then heating the product with water to convert the $C_3N_3Br_3$, which is doubtless formed, into the acid (Merz and Werth). The formation of cyanuric acid from potassium ferrocyanide is explained by the hypothesis that the ferrocyanide contains the radical tricyanogen. There is no evidence of the existence of a radical composed of carbon and nitrogen more complex than C_3N_3. The iron in potassium ferrocyanide is assumed to be bivalent, since the compound is formed by the combination of ferrous cyanide and potassium cyanide.

The foregoing facts lead to the formula

$$\begin{matrix} K_2 = (C_3N_3) \\ K_2 = (C_3N_3) \end{matrix} > Fe,$$
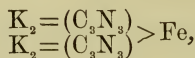
in which the acid radical is ferrocyanogen, $[(C_3N_3)_2Fe]^{IV}$.

The structure of tricyanogen may be

$$\begin{matrix} -C-N=C- \\ \parallel \quad \mid \\ N-C=N \\ \mid \end{matrix} \quad \text{or} \quad \begin{matrix} -N=C=N- \\ \parallel \quad \quad \parallel \\ C=N=C \\ \mid \end{matrix}$$
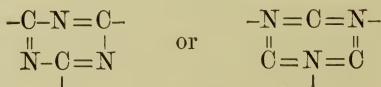
according as the nitrogen in it is considered to be trivalent or pentavalent.

Ferric chloride and potassium cyanide react to form potassium ferricyanide, $K_3(C_3N_3)_2Fe$. Assuming the iron in this salt to be trivalent, we have the structural formula

$$\begin{matrix} K-(C_3N_3) \\ K_2=(C_3N_3) \end{matrix}\!\!\!\rangle\!\!\!= Fe,$$

in which the acid radical is ferricyanogen $[(C_3N_3)_2Fe]^{III}$. Oxidizing agents convert potassium ferrocyanide into ferricyanide, and the latter is changed by reducing agents into ferrocyanide. These reactions are analogous to the changes which ferrous and ferric salts undergo with like treatment.

Potassium Ferrocyanide, $K_4(C_3N_3)_2Fe + 3H_2O$, is known in commerce as yellow prussiate of potash. It is the starting-point in the preparation of most of the cyanides, and is largely used in dyeing. It is manufactured on a large scale by adding a mixture of iron filings or iron oxide and animal substances, such as horn, dried blood, or leather clippings, to molten potassium carbonate. The fused mass after cooling is lixiviated with water, and the solution on evaporating yields crystals of potassium ferrocyanide. The animal matter contains carbon and nitrogen, which react with potassium carbonate to form potassium cyanide. The sulphur in the animal matter, and impure potassium carbonate unites with the iron, forming ferrous sulphide, which reacts with the potassium cyanide to form potassium ferrocyanide, when the fused mass is treated with water.

Potassium ferrocyanide forms yellow crystals, which lose their water of crystallization at 100°, and change to a white powder. The crystals dissolve in two parts of boiling and in four parts of cold water. Potassium ferrocyanide fuses at a red heat, decomposing into potassium cyanide and a compound of carbon and iron.

Ferrocyanic Acid, $H_4(C_3N_3)_2Fe$.—When concentrated hydrochloric acid is added to a cold saturated solution of potassium ferrocyanide, ferrocyanic acid separates in white scales, which may be purified by dissolving in alcohol and then adding ether to reprecipitate the acid. Ferrocyanic acid is a strong acid, capable of decomposing carbonates, acetates, and oxalates. It is an unstable compound, and on exposure to air decomposes with formation of Prussian blue. A number of ferrocyanides are known.

Potassium Ferricyanide, $K_3(C_3N_3)_2Fe$, is commonly known as red prussiate of potash. It is formed when potassium ferrocyanide in solution is treated with reagents which convert ferrous into ferric iron. Thus, when chlorine is passed into a solution of potassium ferrocyanide, potassium ferricyanide and potassium chloride are formed :

$$K_4(C_3N_3)_2Fe + Cl = K_3(C_3N_3)_2Fe + KCl.$$
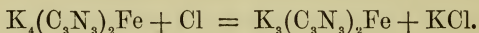
The two salts are separated by repeated crystallization. Potassium ferricyanide forms dark-red crystals. The aqueous solution of the salt is yellowish brown when concentrated, and yellow when dilute. The solution decomposes slightly on long exposure to light, with formation of ferrocyanide and a blue precipitate.

Lead Ferricyanide, $Pb_3,[(C_3N_3)_2Fe]_2 + 16H_2O,$ separates when hot concentrated solutions of potassium ferricyanide and lead nitrate are mixed. More of the salt is deposited on cooling. It is sparingly soluble in cold water.

Ferricyanic Acid, $H_3(C_3N_3)Fe$, is prepared by adding the required amount of sulphuric acid to a solution of the lead salt. The solution filtered from the lead sulphate yields when evaporated at common temperature ferricyanic acid in delicate long brown crystals.

Soluble Prussian Blue, $K(C_3N_3)_2\overset{III}{Fe}\overset{II}{Fe} + Aq.$—When solutions of equal molecules of potassium ferrocyanide and ferric chloride are mixed a blue precipitate is formed. Potassium ferricyanide and ferrous chloride yield the same result. The precipitate in either case is soluble Prussian blue, and, after washing with water to remove the potassium chloride formed, it dissolves in pure water to a blue solution. From this solution it is precipitated by addition of salts. The following equations represent the formation of soluble Prussian blue:

$$\begin{matrix} K> \\ K> \\ K> \\ K> \end{matrix}\begin{matrix}C_3N_3 \\ \\ C_3N_3\end{matrix}\Big>Fe + FeCl_3 = \begin{matrix}K> \\ Fe=\end{matrix}\begin{matrix}(C_3N_3) \\ (C_3N_3)\end{matrix}>Fe + 3KCl;$$
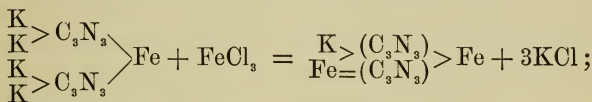
<div style="text-align:center">Potassium ferrocyanide   Soluble Prussian blue</div>

$$\begin{matrix}K> \\ K> \\ K- \end{matrix}\begin{matrix}C_3N_3 \\ \\ C_3N_3\end{matrix}\Big\Rangle Fe + FeCl_2 = \begin{matrix}K- \\ Fe<\end{matrix}\begin{matrix}(C_3N_3) \\ (C_3N_3)\end{matrix}\Big\Rangle Fe + 2KCl:$$
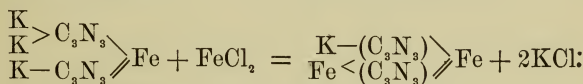
<div style="text-align:center">Potassium ferricyanide   Soluble Prussian blue</div>

The two formulas are evidently identical, each representing ferrous and ferric iron joined to two groups of tricyanogen.

Ferric Ferrocyanide, $Fe_7(CN)_{18}$ or $\overset{III}{Fe_4}[(C_3N_3)_2\overset{II}{Fe}]_3.$—This compound, known as Prussian blue, is obtained as a blue precipitate when potassium ferrocyanide is added to an excess of ferric chloride:

$$3K_4(C_3N_3)_2Fe + 4FeCl_3 = Fe_4[(C_3N_3)_2Fe]_3 + 12KCl.$$
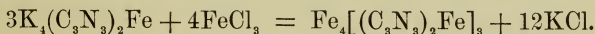
Ferric ferrocyanide is also formed when a ferric salt is added to soluble Prussian blue.

Ferrous Ferricyanide, $Fe_5(CN)_{12}$ or $\overset{II}{Fe_3}[(C_3N_3)_2\overset{III}{Fe}]_2.$—When potassium ferricyanide is added to a ferrous salt a dark-blue precipitate, known as Turnbull's blue, is formed:

$$3FeCl_2 + 2K_3(C_3N_3)_2Fe = Fe_3[(C_3N_3)_2Fe]_2 + 6KCl.$$
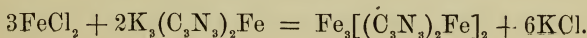
The same compound is obtained by mixing a solution of a ferrous salt with soluble Prussian blue.

Ferrous Thiocyanate, Fe(NCS)$_2$.—Iron dissolves in thiocyanic acid, with formation of ferrous thiocyanate. The salt separates in light-green crystals, containing three molecules of water, when the solution is evaporated out of contact with air. The aqueous solution becomes red on exposure to air.

Ferric Thiocyanate, Fe(NCS)$_3$, is formed and imparts a deep-red color to the solution when solutions of a ferric salt and a thiocyanate are mixed. Solid ferric thiocyanate is obtained by treating a mixture of anhydrous ferric sulphate and potassium thiocyanate with alcohol, which dissolves out ferric thiocyanate, leaving potassium sulphate. The alcoholic solution on evaporation in vacuum deposits dark-red crystals, having the composition $2Fe(NCS)_3 + 3H_2O$. Solutions of ferric thiocyanate become colorless when treated with reducing agents which change ferric iron to ferrous iron.

Exp. 237.—To solutions of a ferrous salt add (*a*) potassium ferrocyanide, (*b*) potassium ferricyanide, (*c*) and ammonium thiocyanate.

Next add the same reagents to solutions of ferric chloride. Note fully the results, and also how ferrous may be distinguished from ferric salts.

The solution of ferrous salt used should be free from ferric salt, and may be prepared by dissolving pure ammonium ferrous sulphate in hot water, which has been previously boiled to expel the air, and then cooling the solution ; or iron wire may be dissolved in hydrochloric acid, and the solution poured into boiled water.

Cobalt, Co.

Atomic Weight, 59.   *Density,* 8.7.

Cobalt is not an abundant element, nor are its ores widely distributed. The pure metal is prepared by igniting the oxide in hydrogen, and the gray powder obtained is melted in

a lime crucible. Cobalt is somewhat more fusible than iron, has the lustre of nickel, is malleable, possesses great tenacity, and is magnetic even at a red heat. Impurities render it brittle and more fusible. It does not tarnish in common air, but oxidizes at a red heat. Electro-deposited cobalt cannot be distinguished in appearance from nickel-plate. Little use has been made of metallic cobalt because of its high cost, but its compounds have long been used for the splendid blue they impart to glass.

Cobalt forms two classes of compounds, viz., cobaltous, containing bivalent cobalt, and cobaltic, which exhibit a higher valence of cobalt. The simple cobaltic salts are unstable.

Cobaltous Chloride, $CoCl_2$ or $Co<_{Cl}^{Cl}$, is obtained in blue scales when chlorine acts on warm powdered cobalt. A solution is prepared by dissolving the carbonate or any of the oxides of cobalt in hydrochloric acid. The solution has a light-red color, which changes to blue on evaporation; dilution with water restores the red color.

Cobaltous Oxide, CoO or $Co=O$, is obtained as an olive-green powder by heating the higher oxides in hydrogen to a temperature not above $300°$.

Cobaltous Hydroxide, $Co(OH)_2$.—Potassium hydroxide produces in solutions of cobaltous salts a blue precipitate of basic salts, which on boiling changes into pale-red cobaltous hydroxide. It rapidly becomes dark brown, owing to formation of cobaltic hydroxide.

Cobaltous Sulphide, CoS or $Co=S$, is obtained as a gray crystalline mass by heating cobalt with sulphur. Ammonium sulphide precipitates a black hydrous sulphide which is insoluble in dilute acids. The sulphides Co_2S_3, Co_2S_4, and CoS_2 are known.

Cobaltous Nitrate, $Co(NO_3)_2$ or $\dfrac{NO_2-O}{NO_2-O}>Co$, is prepared by dissolving the carbonate in nitric acid. The solution when slowly evaporated yields red crystals containing six molecules of water. The salt is a valuable reagent in blow-pipe analysis.

Cobaltous Sulphate, $CoSO_4$ or $SO_2\!<\!\dfrac{O}{O}\!>\!Co$.—A solution of the oxide or carbonate in sulphuric acid deposits, when evaporated at ordinary temperature, red crystals of $CoSO_4 + 7H_2O$, which have the same form as green vitriol. At 40° to 50° crystals of $CoSO_4 + 6H_2O$ separate, which are isomorphous with the hexhydrated magnesium, zinc, and nickel sulphates.

Cobaltous Ammonium Sulphate, $Co(NH_4)_2(SO_4)_2 + 6H_2O$, forms red crystals, which are isomorphous with ferrous ammonium sulphate.

Cobaltous Carbonate, $CoCO_3$, and the hydrate, $CoCO_3 + 6H_2O$, are known. Sodium carbonate produces in hot cobaltous solutions a bluish or violet precipitate of basic carbonates.

Cobaltic Oxide, Co_2O_3 or $O=Co-O-Co=O$, remains as a dark powder when the nitrate is gently ignited.

Cobaltous-Cobaltic Oxide, Co_3O_4 or $O=Co-O-Co-O-Co=O$. —This oxide is formed when either of the other oxides is ignited in air. It is analogous in composition to magnetic oxide of iron.

Cobaltic Hydroxide, $Co(OH)_3$.—Alkali hypochlorites produce in solutions of cobaltous salts a black precipitate of cobaltic hydroxide. This hydroxide and cobaltic oxide dissolve in cold hydrochloric acid to a brown solution (of $CoCl_3$?), which decomposes readily, with evolution of chlorine.

Potassium Cobalticyanide, $K_3(C_3N_3)_2Co$, is an analogue of potassium ferricyanide, with which it is isomorphous. On mixing solutions of potassium cyanide and a cobaltous salt a red precipitate of $Co(CN)_2$ is formed, which dissolves in excess of potassium cyanide as $Co(CN)_2.2KCN$. When a dilute solution of this compound containing an excess of potassium cyanide and some hydrocyanic acid is boiled potassium cobalticyanide is formed:

$$Co(CN)_2.2KCN + KCN + HCN = K_3(C_3N_3)_2Co + H.$$

Cobalticyanic acid is obtained by decomposing the copper salt of it by hydrogen sulphide.

Nickel, Ni.

Atomic Weight, 58. *Density,* 8.9.

Nickel is not an abundant element. The pure metal is obtained by reducing the oxide with hydrogen. It is almost as white as silver, is capable of brilliant polish, is malleable and ductile. The tenacity of nickel exceeds that of iron. Nickel, like iron, combines with carbon and silicon, which render it brittle and more fusible. The cast nickel of commerce also contains copper, cobalt, and iron. Nickel is attracted by the magnet.

Nickel is not changed by long exposure to air, nor tarnished by hydrogen sulphide, and oxidizes only with difficulty at high temperatures. These properties render it a valuable and cheap substitute for silver for plating other metals. Moreover, electro-nickel plate is harder and resists wear better than silver. Nickel-plating is used to prevent iron and steel implements from rusting, and also for ornamenting many articles. The bath best adapted for the deposition of nickel is a solution saturated at ordinary temperature of nickel am-

monium sulphate. To maintain the strength of the solution, and also to prevent its becoming acid, plates of cast nickel are hung in the bath and connected with the positive electrode, the nickel dissolving from the plates as fast as deposited on metallic articles in the bath connected with the negative electrode.

Nickel is largely used in alloys, the most important of which is German silver. This is an alloy of copper, zinc, and nickel, containing 16 to 20 per cent of the latter metal. Alloys of nickel are used for smaller coins; the five-cent pieces of the United States coinage consisting of 1 part of nickel and 3 parts of copper. The same proportion is used in small coins in Germany and Belgium.

Nickel forms but one class of salts, and in these it is bivalent; the oxide, Ni_2O_3, and the sulphide, NiS_2, indicate a higher valence. The hydrous salts are green, and when dehydrated are usually yellowish. Most solutions of nickel are green.

Nickel Chloride, $NiCl_2$ or $Ni<^{Cl}_{Cl}$.—Finely divided nickel burns brilliantly when heated in chlorine, and sublimes in pale golden-yellow scales, which dissolve slowly in water containing hydrochloric acid. Exposed to the air they gradually absorb moisture and become green, and are then easily soluble. A solution of the chloride is best prepared by treating the oxide or carbonate with hydrochloric acid. On concentrating the solution crystals of $NiCl_2 + 6H_2O$ separate, which lose their water on heating. The anhydrous chloride absorbs ammonia, with the formation of $NiCl_2 + 6NH_3$. This compound is also formed when ammonia is added to a solution of the chloride, and separates in blue octahedrons on cooling a hot concentrated solution. When nickel is placed in a solution of ammonium chloride, and connected with the positive electrode of a battery, the metal dissolves slowly. Solutions

thus prepared, containing nickel chloride, ammonia, and ammonium chloride, have been used in nickel-plating.

Nickel Monoxide, NiO or **Ni$=$O**, is obtained as a greenish powder when the hydroxide, carbonate, or nitrate of nickel is intensely ignited. It does not take up oxygen on prolonged heating in air.

Nickel Hydroxide, Ni(OH)$_2$ or **Ni$<^{OH}_{OH}$.**—Sodium or potassium hydroxide produces in solutions of nickel salts a light-green precipitate of nickel hydroxide. It dissolves in ammonia water, forming a solution which has the property of dissolving silk.

Nickel Sesquioxide, N$_2$O$_3$ or **O$=$Ni–O–Ni$=$O**, is prepared by gently igniting nickel nitrate. It is a black powder, which changes into monoxide on heating intensely. It dissolves in hydrochloric acid, with evolution of chlorine, and formation of NiCl$_2$.

Nickel Trihydroxide, Ni(OH)$_3$, is formed when the green nickel hydroxide is suspended in a solution of potassium hydroxide through which chlorine is passed:

$$Ni(OH)_2 + KOH + Cl = Ni(OH)_3 + KCl.$$
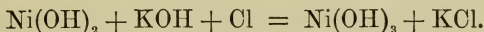
It loses water and oxygen on heating, and behaves with hydrochloric acid like the sesquioxide.

Nickel Nitrate, Ni(NO$_3$)$_2$ or **$^{NO_2-O}_{NO_2-O}>$Ni**, is obtained by dissolving nickel in nitric acid. On evaporating the solution, the salt crystallizes with six molecules of water.

Nickel Cyanide, Ni(CN)$_2$.—On adding potassium cyanide to a solution of a nickel salt, an apple-green precipitate of nickel cyanide is first formed, which dissolves in an excess of potas-

sium cyanide as $Ni(CN)_2.2KCN$. This double salt is decomposed by acids, with separation of nickel cyanide. Nickel does not form compounds analogous to the ferri- and cobalticyanides.

Nickel Sulphate, $NiSO_4$ or $SO_2 <^O_O> Ni$.—This salt is prepared by dissolving the oxide or carbonate in sulphuric acid. If the solution is evaporated at a temperature of 15° to 20°, green crystals of the hydrated salt $NiSO_4 + 7H_2O$ are formed, which are isomorphous with the corresponding salts of zinc and magnesium. At 50° to 70° crystals separate, containing six molecules of water. Hydrous nickel sulphate becomes anhydrous when heated above 280°. Nickel sulphate is very soluble, 100 parts of water at 16° dissolving 37.4 parts, and at 70° 61.9 parts, of $NiSO_4$. The anhydrous sulphate absorbs ammonia gas, forming the compound $NiSO_4.6NH_3$, while from a solution of the sulphate in concentrated ammonia water dark-blue crystals are obtained, having the composition $NiSO_4.4NH_3 + 2H_2O$.

Ammonium Nickel Sulphate, $(NH_4)_2Ni(SO_4)_2 + 6H_2O$.—This salt is manufactured in large quantities for use in nickel-plating by adding ammonium sulphate to a concentrated solution of nickel sulphate. The precipitate which is formed is purified by recrystallization. At 20° 100 parts of water dissolve 5.9 parts, and at 85° 28.6 parts of $(NH_4)_2Ni(SO_4)_2$.

Nickel Carbonates.—Alkali carbonates throw down from solutions of nickel salts a pale-green precipitate of basic carbonates. The metacarbonate $NiCO_3$ is obtained by heating a solution of nickel chloride with calcium carbonate to 150°.

Nickel Monosulphide, NiS, occurs as the mineral millerite, which is sometimes found in hair-like crystals. Nickel monosulphide is obtained artificially by heating together nickel and

sulphur. On adding ammonium sulphide to a solution of a nickel salt a black hydrous sulphide is precipitated.

Nickel Disulphide, NiS$_2$, is obtained in the form of a dark-gray powder by fusing a mixture of nickel carbonate, sodium carbonate, and sulphur, and treating the product with water.

***

Ruthenium, Ru.

Atomic Weight, 103. *Density,* 12.26.

Ruthenium is a brittle, white, difficultly fusible metal. Aqua regia has little action on it, but molten potassium hydroxide containing nitrate attacks it readily. The finely divided metal oxidizes when heated in air.

Ruthenium Dichloride, RuCl$_2$, is formed, together with the trichloride, when the pulverized metal is heated in chlorine; the trichloride volatilizes, leaving the dichloride as a black powder, insoluble in water and acids.

Ruthenium Trichloride, RuCl$_3$.—In order to prepare this chloride an acid is added to a solution of potassium ruthenate, and the precipitate is dissolved in hydrochloric acid. The solution thus obtained yields ruthenium trichloride on evaporation.

Ruthenium Tetrachloride, RuCl$_4$, is obtained by dissolving the tetrahydroxide in hydrochloric acid. It combines with potassium chloride to form the salt K$_2$RuCl$_6$, an analogue of potassium chloroplatinate.

Ruthenium Monoxide, RuO, is obtained by heating the dichloride with sodium carbonate. It is a dark-gray powder, insoluble in acids.

Ruthenium Sesquioxide, Ru$_2$O$_3$, is formed when the finely divided metal is heated in air. It has a dark-blue color, and is insoluble in acids.

Ruthenium Dioxide, RuO$_2$, is formed when the sulphate is intensely heated in air.

Ruthenium Tetroxide, RuO$_4$, sublimes when chlorine is passed into a solution of potassium ruthenate. It melts at 40°, boils at about 100°, and at a little higher temperature decomposes with explosive violence.

Ruthenium Trihydroxide, Ru(OH)$_3$, separates as a dark-brown precipitate on adding potassium hydroxide to a solution of the trichloride.

Ruthenium Tetrahydroxide, Ru(OH$_4$) + 3H$_2$O, is formed when a solution of ruthenium bisulphate is treated with potassium hydroxide, and then evaporated.

Ruthenium Bisulphate, $Ru(SO_4)_2$.—Hydrogen sulphide precipitates RuS_2 from a solution of ruthenium trichloride. This sulphide is converted by nitric acid into bisulphate, which remains as a deliquescent yellow powder on evaporating the solution.

Potassium Ruthenate, K_2RuO_4, is formed when finely divided ruthenium is fused with potassium hydroxide mixed with nitre. Its aqueous solution is reddish yellow.

Potassium Perruthenate, $KRuO_4$, is prepared by acting on the preceding salt with chlorine :

$$K_2RuO_4 + Cl = KRuO_4 + KCl.$$
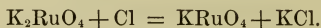
From the green solution thus obtained black crystals separate, isomorphous with potassium permanganate.

Potassium Ruthenocyanide, $K_4(C_3N_3)_2Ru + 3H_2O$, is isomorphous with potassium ferrocyanide.

Rhodium, Rh.

Atomic Weight, 104.   *Density,* 12.1.

Rhodium is a very hard grayish metal, less ductile and fusible than platinum. The metal oxidizes at a red heat, best in form of powder. It is not attacked by acids, but if alloyed with lead or platinum it dissolves in aqua regia.

Rhodium Trichloride, $RhCl_3$, is the only known halide of rhodium. It is formed when the metal is heated in chlorine. It is insoluble in acids, even aqua regia, and only gives up its chlorine at a red heat.

Rhodium Monoxide, RhO, is obtained as a dark powder when $Rh(OH)_2$ is heated.

Rhodium Sesquioxide, Rh_2O_3, is obtained by heating the nitrate.

Rhodium Trihydroxide, $Rh(OH)_3$.—When a solution of Na_3RhCl_6 is heated with a concentrated solution of potassium hydroxide a black precipitate of rhodium trihydroxide is formed. It is insoluble in acids. If a cold dilute solution of potassium hydroxide is used, another modification is obtained, which is soluble in acids and potassium hydroxide.

Rhodium Dioxide, RhO_2, is insoluble in acids. It is formed by repeated fusion of the finely divided metal with potassium hydroxide and nitrate.

Rhodium Tetrahydroxide, $Rh(OH)_4$, is formed by the prolonged action of chlorine on an alkaline solution of the trihydroxide. It dissolves in

hydrochloric acid to a blue solution, which slowly gives off chlorine, and changes to a red color.

Sodium Rhodium Chloride, Na₃RhCl₆, is prepared by heating a mixture of rhodium and common salt in chlorine. It is soluble, and crystallizes with 12 molecules of water. The corresponding ammonium salt separates when a solution of rhodium chloride and ammonium chloride evaporates spontaneously.

Rhodium Nitrate is obtained as a gummy mass by evaporating a solution of rhodium hydroxide in nitric acid.

Rhodium Sulphate, Rh₂(SO₄)₃, separates in hydrous crystals when a solution of rhodium hydroxide in sulphuric acid is evaporated.

Palladium, Pd.

Atomic Weight, 106. *Density,* 12.

Palladium is a white metal resembling platinum and silver in lustre and color. It is the most fusible of the platinum metals. It welds at a red heat more easily and is softer and more malleable than platinum. It volatilizes in the oxyhydrogen flame, giving off green vapors, which condense to a dust consisting of oxide and metal. At a red heat the metal becomes covered with a blue film of oxide, which disappears at higher temperatures. Palladium dissolves in hot nitric acid, more readily if it contains nitrous acid. Hydrochloric acid dissolves palladium sponge in contact with air. The metal is but little used in the arts. On account of its retaining its lustre in air it has been used for the graduated surfaces of instruments.

Palladium Hydride.—Palladium possesses greater power of absorbing hydrogen than any other metal. At common temperatures palladium foil absorbs upwards of 370 volumes of the gas, and at 100° about 650 volumes. When palladium is made the negative electrode in dilute sulphuric acid it takes up as much as 960 volumes of hydrogen. The compound retains the appearance of the metal, is tough, and more mag-

hydrochloric acid to a blue solution, which slowly gives off chlorine, and changes to a red color.

Sodium Rhodium Chloride, Na_3RhCl_6, is prepared by heating a mixture of rhodium and common salt in chlorine. It is soluble, and crystallizes with 12 molecules of water. The corresponding ammonium salt separates when a solution of rhodium chloride and ammonium chloride evaporates spontaneously.

Rhodium Nitrate is obtained as a gummy mass by evaporating a solution of rhodium hydroxide in nitric acid.

Rhodium Sulphate, $Rh_2(SO_4)_3$, separates in hydrous crystals when a solution of rhodium hydroxide in sulphuric acid is evaporated.

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Atomic Weight, 106. *Density,* 12.

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netic than pure palladium. According to some investigators the two elements form the compound Pd_2H, which takes up more hydrogen. Palladium hydride gives up all its hydrogen at 100° in vacuum, and also when ignited.

Palladium forms two classes of compounds, viz., palladious and palladic. The simple salts of the common acids are palladious compounds; palladic salts doubtless exist in solution, but they easily change to palladious salts.

Palladious Chloride, $PdCl_2$.—When a solution of palladium in aqua regia is evaporated this compound remains as a brown mass. It fuses at a red heat, loses half its chlorine, and changes to palladium monochloride, $PdCl$.

Palladious Iodide, PdI_2, is formed by the direct union of its elements. Palladium is blackened when tincture of iodine is evaporated upon it. Potassium iodide produces in solutions of palladious chloride a black precipitate of palladious iodide; a very characteristic reaction.

Palladious Oxide, PdO, remains as a black powder when the nitrate is heated. Alkali carbonates precipitate from solutions of palladious salts a hydroxide, or possibly a basic carbonate, soluble in acids. The precipitate is converted at a faint red heat into the oxide Pd_2O. All the palladium oxides are completely decomposed on intense ignition. Sulphides analogous to the above oxides are known, also PdS_2.

Palladious Nitrate, $Pd(NO_3)_2$, is prepared by dissolving the metal in nitric acid. It is very deliquescent.

Palladious Sulphate, $PdSO_4$, is obtained by dissolving the metal in sulphuric acid containing a little nitric acid. It is decomposed by water into a basic salt.

Palladic Oxide, PdO_2, is formed when ammonium palladic chloride is boiled with potassium hydroxide. It dissolves in

hot dilute hydrochloric acid, with evolution of chlorine, and formation of $PdCl_2$.

Palladic Chloride, $PdCl_4$, has not been isolated. The aqua regia solution of the metal doubtless contains hydrogen palladic chloride, H_2PdCl_6.

Potassium Palladic Chloride, K_2PdCl_6.—This salt is obtained when an aqua regia solution of palladium is treated with potassium chloride and then evaporated. It is insoluble in alcohol and in a solution of potassium chloride.

Osmium, Os.

Atomic Weight, 192? *Density,* 22.5.

This element is remarkable for its density, which is greater than that of any other substance. Metallic osmium is obtained in the form of a powder by passing the vapor of the tetroxide mixed with carbon monoxide and dioxide through a hot porcelain tube. Crystalline osmium is formed when amorphous osmium is fused with tin. The latter metal is removed by hydrochloric acid, and the crystals are finally heated in dry hydrochloric acid gas. The pure metal has a fine blue color, crystallizes in cubes or rhombohedrons nearly like cubes, which are harder than glass. Osmium volatilizes without melting when exposed in a lime furnace to the intense heat of the oxyhydrogen flame. Amorphous osmium which has not been intensely ignited is soluble in aqua regia and nitric acid. The metal is not used in the arts, but iridosmine, a native alloy of iridium and osmium, is valued for points to gold pens.

Osmium in its highest oxide has a valence of eight, other compounds exhibit a lower valence.

Osmium Trichloride, $OsCl_3$, is known only in combination with other chlorides, as for example, $3KCl.OsCl_3 + 3H_2O$.

Osmium Tetrachloride, $OsCl_4$, is obtained in the form of a red sublimate when the metal is heated in dry chlorine. The concentrated aqueous solution is yellow, the dilute green. The solution decomposes on standing, lower oxides separating, and hydrochloric acid and osmium tetroxide remaining in the solution.

Potassium Chlorosmate, K_2OsCl_6, crystallizes out when a solution con-

taining potassium chloride, hydrochloric acid, and osmium tetroxide is evaporated. It is soluble in water and insoluble in alcohol.

The **Osmium Oxides** are OsO, Os_2O_3, OsO_2, and OsO_4.

Osmium Tetrahydroxide, $Os(OH)_4$, separates as a black precipitate when alcohol is added to an aqueous solution of the tetroxide. It forms unstable salts.

Osmic Acid, H_2OsO_4, has not been isolated, but a number of its salts have been prepared.

Potassium Osmate, $K_2OsO_4 + 2H_2O$, is obtained by dissolving the tetroxide in a solution of potassium hydroxide and adding alcohol. It crystallizes in dark-red octahedrons.

Osmium Tetroxide, OsO_4, is commonly known as osmic acid. It is formed when the metal is burned in air, or is oxidized by nitric acid. The tetroxide is soft, crystalline, and volatile at ordinary temperature. It melts at a gentle heat, and boils at 100°. Its gas density has been found by experiment to be 128.5; theory requires 131 for OsO_4. Osmium tetroxide is very poisonous. Its aqueous solution does not redden litmus, and is valuable in microscopy for coloring animal tissues.

Osmiocyanic Acid, $H_4(C_3N_3)_2Os$, separates on addition of hydrochloric acid to a solution of its potassium salt.

Potassium Osmiocyanide, $K_4(C_3N_3)_2Os + 3H_2O$, is an analogue of potassium ferrocyanide.

Iridium, Ir.

Atomic Weight, 193. *Density,* 22.4.

The metal is obtained in a gray porous mass, similar to platinum sponge, by heating ammonium iridic chloride. It may be fused in a lime furnace with an oxyhydrogen flame, but coal-gas and oxygen will not answer. Fused iridium has the lustre of polished steel. It is harder than platinum, is only slightly malleable, and breaks with a fine-grained fracture. Iridium black separates as an impalpable powder when an alcoholic solution of iridium sulphate is exposed to sunlight. It is more active in causing the union of combustible gases with oxygen than platinum black. Fused iridium is soluble in no acid, but when alloyed with much platinum dissolves in aqua regia. Molten alkali hydroxides and potassium disulphate attack iridium, and chlorine combines with it at a red heat.

Iridium forms two series of compounds corresponding to iridious chloride, $IrCl_3$, and iridic chloride, $IrCl_4$. The metal appears to be

bivalent in IrS and in $IrSO_3$, the latter having been obtained in combination with sodium sulphite and other salts.

Iridious Chloride, $IrCl_3$, sublimes when iridium is heated in chlorine. A solution of this chloride is prepared by treating iridic chloride with sulphur dioxide.

Potassium Irido-chloride, $K_3IrCl_6 + 3H_2O$, is obtained by reducing potassium chloriridate with hydrogen sulphide. The solution after addition of potassium chloride yields green crystals on evaporation.

Iridious Oxide or Iridium Sesquioxide, Ir_2O_3, is formed when iridium black or sponge is ignited in air. It is completely decomposed at temperatures above 1000°.

Irido-potassium Sulphate, $Ir_2(SO_4)_3 + 3K_2SO_4$.—This double salt remains as a green powder when an iridium compound is fused with potassium disulphate and the product is treated with a solution of potassium disulphate. It is soluble in water and dilute sulphuric acid.

Iridic Chloride, $IrCl_4$.—A solution of iridic hydroxide in hydrochloric acid, or of iridium black in aqua regia, probably contains chloriridic acid, H_2IrCl_6. The solution is said to leave the tetrachloride when evaporated at not above 40°.

Potassium Chloriridate, K_2IrCl_6, is obtained by adding potassium chloride to a solution of iridic chloride. It is sparingly soluble in cold water and insoluble in alcohol.

Iridic Hydroxide, $Ir(OH)_4$.—On addition of an alkali hydroxide to a solution of iridic chloride a dense blue precipitate of iridic hydroxide is formed.

Iridic Oxide, IrO_2, is a heavy black powder obtained by heating iridic hydroxide. It is insoluble in acids.

Iridicyanic Acid, $H_3(C_3N_3)_2Ir$, and **Potassium Iridicyanide, $K_3(C_3N_3)_2Ir$**, have been prepared.

The Iridium Sulphides are IrS, Ir_2S_3, and IrS_2.

Platinum, Pt.

Atomic Weight, 195. *Density,* 21.5.

Platinum is almost as white as tin, is moderately hard and tenacious, and ranks next to gold and silver in malleability and ductility. It may be drawn into fine wire or rolled into thin sheets. It is infusible in a wind furnace and in the flame of a Bunsen burner or blast-lamp; but very fine platinum

wire may be fused in a blow-pipe flame, and also in the under-edge of an illuminating-gas jet.

Platinum is not oxidized when heated in air or oxygen, nor is it attacked by any single acid. The most common solvent for the metal is aqua regia, in which it is slowly soluble. Liquids containing free chlorine also dissolve it. Platinum is not affected by molten potassium or sodium carbonates, but it is attacked when nitre, the alkali hydroxides, cyanides, or sulphides are fused in contact with it.

Metallic platinum is obtained by igniting ammonium chloro-platinate in the form of a gray porous mass known as platinum sponge, which may be welded when red-hot into compact metal, or fused in a lime crucible by means of a blow-pipe flame supplied with coal gas and oxygen.

When platinum is precipitated from solutions by a reducing agent it is obtained as a very fine powder known as platinum black. Platinum, like other solids, condenses gases on its surface, and it possesses in a marked degree the property of causing the union of oxygen with combustible gases. Platinum black condenses over 800 times its volume of oxygen; platinum sponge also condenses the gas, but not in such quantity.

Platinum, on account of its infusibility and permanence when in contact with acids, alkaline solutions, or molten alkali carbonates, is indispensable to the chemist for crucibles, dishes, and other apparatus. Gold also resists the action of chemicals, but it costs three to four times as much as platinum, and is moreover too fusible for many purposes. Platinum is used in the chemical industry for the large stills required in the concentration of sulphuric acid, for evaporating dishes, and other purposes. An alloy of platinum containing several per cent of iridium is harder and less readily attacked by various reagents than pure platinum, and such an alloy is commonly employed for platinum apparatus.

Platinum occurs alloyed with small quantities of the plati-

num metals, and is found in minute traces in some minerals and in most silver. Little was known about it until the middle of the last century, and the metal did not come into use until the present century, when the increased knowledge of chemistry made it possible to purify and work it.

Platinum forms two series of compounds, viz., the platinous, containing bivalent platinum, as in $PtCl_2$; and the platinic compounds, containing tetravalent platinum, as in $PtCl_4$.

Platinous Chloride, $PtCl_2$ or $Pt{<}{Cl \atop Cl}$, is obtained by heating chloroplatinic acid to 300°, as a grayish-green powder, which leaves metallic platinum on ignition. Platinous chloride is insoluble in water, but soluble in hot hydrochloric acid, with formation of chloroplatinous acid, H_2PtCl_4. A number of salts of this acid have been prepared, as, for example, potassium chloroplatinite, K_2PtCl_4, and calcium chloroplatinite, $CaPtCl_4 + 8H_2O$.

Platinous Oxide, PtO.—When platinous hydroxide is cautiously heated the oxide is obtained as a gray powder, which is reduced to the metal on ignition.

Platinous Hydroxide, $Pt(OH)_2$, is precipitated when sodium hydroxide is added to a solution of potassium chloroplatinite. It is a weak base.

Platinum Tetrachloride, Platinic Chloride, } $PtCl_4$ or $Pt{=}\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}$ — This compound, in the hydrous state, is prepared by adding the amount of silver nitrate required to separate one third of the chlorine from chloroplatinic acid, and evaporating at ordinary temperature the solution filtered from the silver chloride formed, when large red crystals will be obtained, having the composition $PtCl_4 + 5H_2O$. This substance loses

four molecules of water at 100°, but all of the water cannot be expelled without decomposing the salt.

Potassium Platinonitrite, $K_2Pt(NO_2)_4$, is an example of a series of compounds which do not appear to be double salts. It is obtained by acting on potassium chloroplatinite with potassium nitrite. Hydrogen sulphide fails to precipitate platinum sulphide from its solution.

Chloroplatinic Acid, H_2PtCl_6, crystallizes with six molecules of water in brownish-red deliquescent prisms from a solution of platinum in aqua regia which has been repeatedly evaporated with hydrochloric acid to remove all nitric acid. This compound is also called platinum or platinic chloride. Chloroplatinic acid readily exchanges its hydrogen for metals, forming a series of salts known as chloroplatinates or platinichlorides.

Potassium Chloroplatinate, K_2PtCl_6, separates on addition of potassium hydroxide or a potassium salt to a solution of chloroplatinic acid as a yellow crystalline powder. It crystallizes from hot water in small reddish-yellow octahedrons. At ordinary temperature 100 parts of water dissolve about 1 part, and at 100° 5.18 parts of the salt. It is insoluble in alcohol, and in a saturated solution of potassium chloride.

Sodium Chloroplatinate, Na_2PtCl_6 is easily soluble in water and alcohol. It crystallizes with six molecules of water, which it loses at 100°.

Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$, is prepared by adding ammonium chloride to a solution of chloroplatinic acid. It crystallizes in octahedrons similar in appearance to the potassium salt. It is less soluble in water than the latter, is but slightly soluble in a solution of ammonium chloride, and is insoluble in alcohol.

Platinic Hydroxide, Pt(OH)$_4$, possesses both basic and acid properties, dissolving in dilute acids, and in a solution of sodium hydroxide. It is converted into PtO$_2$ by gentle heat.

Platinic Sulphate, Pt(SO$_4$)$_2$, is obtained by evaporating a solution of the hydroxide or chloride in sulphuric acid.

Platinous Sulphide, PtS, and **Platinic Sulphide, PtS$_2$,** have been prepared.

Platinum Amines.—There are a large number of very complex compounds of platinum and ammonia whose hydroxides are strong bases which form well-defined salts. The other platinum metals also form amine compounds.

Exp. 238.—*a.* Dissolve a gram or more of thin scrap platinum in warm aqua regia. Evaporate the solution on a water bath to dryness, add some hydrochloric acid to the residue, and repeat the evaporation. Dilute with water, so that each cubic centimeter of solution shall contain 0.05 gram of platinum.

b. To 5 cc of the solution add an excess of a solution of ammonium chloride. Collect the ammonium chloroplatinate on a filter, dry, and ignite cautiously in a covered porcelain crucible.

c. Hold a piece of the platinum sponge in a small jet of hydrogen. The metal will glow, owing to the combination of oxygen condensed from the air and the hydrogen by the metal. The Döbereiner lamp consists of a small hydrogen generator for supplying a jet of hydrogen which is ignited by platinum sponge.

d. After using the platinum sponge in the above experiment, heat it intensely in the blast-lamp flame. It will not now act so energetically when hydrogen comes into contact with it.

Summary of the Eighth Group.

This group of elements contains three well-defined subgroups, which fall in three different periods of Mendelejeff's classification. The atomic weights, densities, and atomic vol-

umes of the members of the group are given in the following table :

		Atomic weight.	Density.	Atomic volume
Of period II.	Iron, . . .	56	7.8	7.2
	Cobalt, . . .	59	8.7	6.8
	Nickel, . . .	58	8.9	6.5
Of period III.	Ruthenium, .	103	12.2	8.4
	Rhodium, . .	104	12.1	8.6
	Palladium, .	106	12	8.8
Of period V.	Osmium, . .	192	22.5	8.5
	Iridium, . .	193	22.4	8.6
	Platinum, . .	195	21.5	9.

The elements of each sub-group differ but little in their atomic weights, densities, and atomic volumes. Ruthenium, rhodium, and palladium are often called the light platinum metals, in distinction from the heavy platinum metals, which are osmium, iridium, and platinum. The atomic weights and densities of the light platinum metals are little more than half the magnitude of the corresponding constants of the heavy platinum metals. Accordingly we find that the atomic volumes of the platinum metals differ but little. The atomic weights of iron, cobalt, and nickel bear to those of the light platinum metals a relation similar to that stated between the two classes of platinum metals. The densities of iron, cobalt, and nickel are somewhat higher in comparison with their atomic weights, and hence the atomic volumes are lower than those of the platinum metals.

The metals of the group are hard and white, or nearly white, osmium excepted, which has a blue color. The members of a sub-group, as might be expected, present analogies in chemical properties, and all the nine elements of the eighth group are more or less closely related chemically. This is partly shown in the following tables of compounds :

HALIDES.

Iron, ... $FeCl_2$	$FeCl_3$	
Cobalt, ... $CoCl_2$	$CoCl_3$?	
Nickel, ... $NiCl_2$		
Ruthenium, ... $RuCl_2$	$RuCl_3$	$RuCl_4$
Rhodium, ...	$RhCl_3$	
Palladium, ... $PdCl_2$		$PdCl_4$
Osmium, ...	$OsCl_3$?	$OsCl_4$
Iridium, ...	$IrCl_3$	$IrCl_4$
Platinum, ... $PtCl_2$		$PtCl_4$

OXIDES.

Iron, ... FeO	Fe_8O_4	Fe_2O_3	
Cobalt, ... CoO	Co_3O_4	Co_2O_3	
Nickel, ... NiO		Ni_2O_3	
Ruthenium, . . . RuO		Ru_2O_3	RuO_2	$RuO_.$
Rhodium, ... RhO		Rh_2O_3	
Palladium, . . . PdO			PdO_2
Osmium, ... OsO		Os_2O_3	OsO_2	OsO_4
Iridium, ...		Ir_2O_3	IrO_2
Platinum, ... PtO			PtO_2

OXYGEN SALTS.

Iron, ... $FeSO_4$	$Fe_2(SO_4)_3$	K_2FeO_4	
Cobalt, ... $CoSO_4$			
Nickel, ... $NiSO_4$			
Ruthenium, . . .		$Ru(SO_4)_2$	K_2RuO_4 $KRuO_4$
Rhodium, ...	$Rh_2(SO_4)_3$		
Palladium, . . . $PdSO_4$			
Osmium, ...		K_2OsO_4	
Iridium, ...	$Ir_2(SO_4)_3$		
Platinum		$Pt(SO_4)_2$	

COMPLEX CYANIDES.

Iron, ... $K_4(C_3N_3)_2Fe$	$K_3(C_3N_3)_2Fe$	
Cobalt, ... ——	$K_3(C_3N_3)_2Co$	
Nickel, ... ——	——	
Ruthenium, ... $K_4(C_3N_3)_2Ru$	——	
Rhodium, ... ——	——	
Palladium, ... ——	——	
Osmium, ... $K_4(C_3N_3)_2Os$	——	
Iridium, ... ——	$K_3(C_3N_3)_2Ir$	
Platinum, ... ——	——	

There are other series of complex compounds which have not been described in this book, and therefore cannot well be used in the study of the group. A more extended discussion than space allows would show marked resemblance between iron, ruthenium, and osmium ; between cobalt, rhodium, and iridium ; and between nickel, palladium, and platinum.

Iron, cobalt, and nickel possess strongly basic properties, forming stable oxygen salts. Ferric salts are more permanent than ferrous, while the reverse is the case with cobaltic and cobaltous salts ; and nickel forms only nickelous salts. The platinum metals are feebly basic, forming unstable oxygen salts, and their higher oxides and hydroxides exhibit towards strong bases an acidic character. The tetroxides of ruthenium and osmium appear to be neutral bodies, possessing neither acidic nor basic properties. The compounds of the platinum metals with non-metals are more or less readily decomposed by heat, while the compounds of iron, cobalt, and nickel resist intense ignition, or are reduced to oxides.

THE ATOMIC THEORY.

In the introduction certain physical phenomena have been explained by the theory that matter is composed of discrete particles called molecules. These are physical units, or smallest particles which take part in physical changes. We have seen that molecules are divisible into parts, as, for example, those of hydrogen and chlorine, page 61. These parts have been termed *atoms*, and we have taken for granted that matter is composed of atoms; and further, that there is one fundamental difference between different kinds of matter which cannot be resolved into simpler forms, i.e., a difference in the masses of the atoms, or, as commonly stated, a difference in atomic weights.

The quantitative determinations made in our experiments have given results in accord with the view that one kind of matter always takes part in chemical changes in a definite ratio or a simple multiple thereof. Further, we have become familiar with a large number of reactions represented by equations in which the relative weights of different kinds of matter taking part in the changes are represented. The equations, unless hypothetical, are based upon determinations of the quantities reacting.

Philosophers have held different views regarding the divisibility of matter; some maintaining that it is continuous and capable of infinite division, and others that it is composed of particles which cannot be resolved into smaller parts. A knowledge of the formation of compounds from unlike substances led to the hypothesis that chemical union results from

the combination of unlike particles.   At the beginning of the
present century the particles of different kinds of matter were
supposed to differ in weight.   This was Dalton's hypothesis,
and is the basis of the atomic theory of the present time.   It
was first suggested to him by his investigations of marsh gas
and olefiant gas, two compounds of carbon and hydrogen,
which have the following composition, expressed centesimally:

	Marsh gas.	Olefiant gas.
Carbon, ...	75	85.7
Hydrogen, ...	25	14.3

On comparing the results he saw that in marsh gas the
mass of the hydrogen is one third that of the carbon, and in
olefiant gas it is one sixth.   He then found that other com-
pounds exhibit similar relations, as for example the oxides of
carbon and the oxides of nitrogen.   The oxides of carbon have
the composition—

	Carbon monoxide.	Carbon dioxide.
Carbon, ...	42.86	27.27
Oxygen, ...	57.14	72.73

Here the quantity of oxygen in the first is one and one third
times that of the carbon, and in the second two and two thirds
times.

Such data led Dalton to the

Law of Multiple Proportions.— *When two elements combine
in different proportions, the weight of one element increases
by simple multiples, the weight of the other element being re-
garded as constant.*

Dalton sought for an explanation of the fact that two ele-
ments may combine to form different compounds.   He sup-
posed that all substances are made up of indivisible particles,
called *atoms*, which cannot be divided, and that compounds
result from the approximation of atoms of different kinds.

He therefore concluded that one atom of an element may unite with one, two, or more atoms of another element; and since atoms of one kind have a definite weight, the several compounds which result from the combination of two elements will contain each element in proportion to its atomic weight or a simple multiple thereof.

The atomic theory has developed with the advance of science, and much has been learned regarding the various properties of atoms. We shall only state those which are of fundamental importance in chemistry. According to the atomic theory atoms are indivisible; atoms of different kinds differ in mass; all atoms of one kind of matter possess the same mass and identical properties. In other words, the atoms of an element are alike in all respects, and the atoms of different elements differ in mass, and more or less in chemical properties.

Law of Definite Proportions. — *The proportions by weight of the constituents of a chemical compound are invariable.*

This law is based on a vast number of analyses and syntheses of well-known compounds, whose composition has been found to be constant within the limits of the errors of experiment.

Let us consider how the law supports the theory that the atoms of an element all have the same weight. For example, we will suppose that the atoms of oxygen differ in weight. In such case we might expect that sometimes the lighter atoms would exceed the heavier in a given quantity of water formed synthetically by the union of hydrogen with oxygen. Then we should have a sample of water with less than $\frac{8}{9}$ of its weight of oxygen. The numerous syntheses of water have given no such result. Since water formed by burning hydrogen with varying proportions of oxygen, and by various chemical decompositions, possesses constant composition and properties,

we conclude that the atoms of oxygen composing it do not vary from each other in any respect, and that the same is true of the atoms of hydrogen.

Determination of Atomic Weights.

Before considering the methods for finding atomic weights we need to have clearly in mind what an atomic weight represents. It is defined on page 47 thus :

An atomic weight is a number expressing the ratio of the mass of the smallest part of an element entering into combination to the mass of an atom of hydrogen, or half the molecule of hydrogen.

We observe that an atomic weight does not represent the weight of an atom, but, on the contrary, represents the relative mass of an atom compared to the mass of an atom of hydrogen, which is taken as unity. The absolute mass of an atom is far too small to be determined by chemical methods; but the ratio of the mass of an element entering into combination to the mass of hydrogen also entering into combination is known, in case of many of the elements, with a very considerable degree of accuracy. The determination of the atomic weights of elements which form gasifiable compounds, i.e. compounds of which the molecular weights can be determined, involves—

1st. The experimental determination of the ratios of the mass of an element entering into the compound molecules to the mass of the atom of hydrogen ; and,

2d. Finding the smallest of these ratios.

For example, we may take the following compounds of chlorine :

	Gas density.	Molecular weight.	Composition.
Hydrogen chloride,	18.25	36.5	Hydrogen 1, Chlorine 35.5.
Methyl chloride,	25 25	50.5	Carbon 12, Hydrogen 3, Chlorine 35.5.
Methylene chloride,	42.5	85	Carbon 12, Hydrogen 2, Chlorine 71.
Chloroform,	59.75	119.5	Carbon 12, Hydrogen 1, Chlorine 106.5.

Here the first column gives the observed gas density, the second the molecular weight as deduced by the law of Avogadro, and the third the composition derived from analysis. Evidently the smallest ratio of the mass of chlorine in the molecules of the above compounds to the mass of the atom of hydrogen is 35.5 : 1. Many other compounds of chlorine are known, and in none is a smaller ratio found. Hence we conclude that 35.5 is the maximum atomic weight of chlorine. If compounds of chlorine are discovered in which the ratio is less than now known, then 35.5 will be proved to be a multiple of the true atomic weight.

For the atomic weight of oxygen we have—

	Gas density.	Molecular weight.	Composition.
Water,	9	18	Hydrogen 2, Oxygen 16.
Methyl alcohol,	16	32	Hydrogen 4, Carbon 12, Oxygen 16.
Ethyl alcohol,	23	46	Hydrogen 6, Carbon 24, Oxygen 16.
Acetic acid,	30	60	Hydrogen 4, Carbon 24, Oxygen 32.

The smallest ratio of the mass of oxygen in these compounds to the mass of the atom of hydrogen is 16 : 1. From a consideration of the carbon compounds in the foregoing tables we conclude that 12 is the atomic weight of carbon.

To illustrate further, we will take the compounds of carbon and oxygen :

	Gas density.	Molecular weight.	Composition.
Carbon monoxide,	14	28	Carbon 12, Oxygen 16.
Carbon dioxide,	22	44	Carbon 12, Oxygen 32.

Accordingly, we have carbon 12 and oxygen 16, numbers identical with those deduced from the hydrogen compounds of these elements. The atomic weights of chlorine, oxygen, and carbon are founded upon the composition and molecular weights of a very large number of their compounds, but the foregoing examples suffice for illustration.

A number of the elements do not form gasifiable compounds, hence the molecular weights of their compounds are unknown. The relative masses, which exist in the compounds of such an element with elements whose atomic weights are known, are found by analysis and synthesis, and the number which is the true atomic weight is found by the

Law of Dulong and Petit.—*The specific heat of an element in the solid state multiplied by its atomic weight is nearly constant.*

For example:

	Specific heat.	Atomic weight.	Sp. ht. × at. wt.
Aluminum,	0.225	27	6.1
Iron,	0.114	56	6.4
Lead,	0.0314	207	6.5
Magnesium	0.25	24	6.0

To illustrate the application of this law in fixing an atomic weight, let us take as an example calcium. It was found that 20 weights of this metal combine with 35.5 weights of chlorine, with 8 weights of oxygen, and displace 1 weight of hydrogen from acids in forming salts. All the reactions of calcium can be accounted for by assuming that 20 is its combining weight. It is easy to see that half or double this number will answer equally well. Bunsen found the specific heat of metallic calcium to be 0.17. Therefore, since of these possible values for the atomic weight 40 is the only one which, multiplied by the specific heat, will give nearly 6, we conclude that the atomic weight of calcium is 40.

Let us next consider the atomic weights of elements, for-tunately few, which do not form gasifiable compounds, and whose specific heats are doubtful or unknown. In such case we compare the compounds of the elements in question with those of closely related elements whose atomic weights are known. For example, calcium, strontium, and barium are very similar in chemical deportment, forming compounds which possess remarkable similarity in properties. They form a clearly-defined group of elements, and in all probability their compounds have an analogous composition. Strontium chloride contains 43.75 weights of strontium and 35.5 weights of chlorine. Its composition may therefore be represented by the formula $SrCl$. But the formula of calcium chloride is $CaCl_2$, and from analogy for the corresponding strontium salt we have $SrCl_2$, which requires 87.5 weights of strontium to twice 35.5 weights of chlorine. In the same way we may compare other classes of calcium and strontium compounds, and we conclude that 87.5 is the probable atomic weight of strontium. The atomic weight of barium rests upon the same basis as that of strontium.

We have seen that atomic weights of some elements are not directly compared in the experimental data to the mass of the atom of hydrogen, but to the mass of some other element whose relation to the atom of hydrogen is known. In fact, most of the atomic weights are based upon such indirect com-parisons.

In concluding the discussion, let us endeavor to obtain a clear conception of the data required to fix an atomic weight.

1. The proportion by weight of the element must be de-termined with the greatest possible accuracy by analysis or synthesis, or both, in compounds which can best be prepared in greatest purity. Such compounds should also be of the element in question with elements whose atomic weights are most accurately known.

2. The determination of the gas density, if possible, of one or more compounds of the element.

3. The determination of the specific heat of the element in the solid state.

Do Atoms Exist?—This may be regarded as a fundamental question in chemistry and physics. The present science of chemistry is based upon the atomic theory. Without it we have no explanation of the law of definite proportions, the law of multiple proportions, and the fact that isomeric compounds exist. We believe that chemical changes are due to combinations of atoms, the separation of groups of atoms, and also to the rearrangement of atoms within a molecule. If, then, the atomic theory is in accord with all facts and laws of physical and chemical science, we must conclude that atoms exist. It is often stated that atoms are so small that it is not possible to prove their existence. Until, however, facts are discovered which are clearly at variance with the atomic theory it must be regarded as established.

THE PERIODIC LAW.

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THE study of successive groups of elements has made evident the arrangement in Mendelejeff's classification. The table, p. 49, presents the elements in order of increasing atomic weights, and in groups containing elements more or less closely related in properties. The members of a group are also arranged in order of their increasing atomic weights; e.g., the first group containing Li, 7; Na, 23; K, 39; Cu, 63.3; Rb, 85.5; Ag, 107.9; Cs, 133; and Au, 196. The remarkable fact presents itself that the atomic weight of any member of this group is approximately a numerical mean of the next lower and next higher atomic weight, omitting the last; thus:

$$\frac{7 + 39}{2} = 23, \quad \frac{23 + 63.3}{2} = 43, \quad \frac{39 + 85.5}{2} = 62.3,$$

$$\frac{63.3 + 107.9}{2} = 85.6, \quad \frac{85.5 + 133}{2} = 109.2.$$

Such relations between the atomic weights of the elements of a natural group have long been known.

It has been shown in the summaries of the groups that the properties of the members of a group vary with more or less regularity with the atomic weights,

Let us now consider some of the simplest relations which appear when the elements are arranged according to increasing atomic weights, and take for this purpose the following table :

Li = 7	LiCl	Li$_2$O	Na = 23	NaCl	Na$_2$O
Be = 9	BeCl$_2$	BeO	Mg = 24	MgCl$_2$	MgO
B = 11	BCl$_3$	B$_2$O$_3$	Al = 27	AlCl$_3$	Al$_2$O$_3$
C = 12	CH$_4$	CO$_2$	Si = 28	SiH$_4$	SiO$_2$
N = 14	NH$_3$	N$_2$O$_5$	P = 31	PH$_3$	P$_2$O$_5$
O = 16	OH$_2$		S = 32	SH$_2$	SO$_2$
F = 19	FH		Cl = 35.5	ClH	

The capacity to combine with chlorine or hydrogen increases regularly from lithium to carbon, and then diminishes regularly to fluorine. Following fluorine is sodium, which, like lithium, combines with one atom of chlorine, and also forms an oxide analogous to lithium oxide. From sodium to silicon the number of fixed atoms of hydrogen or chlorine increases regularly, and then diminishes from silicon to chlorine. It is obvious that in this respect there is complete analogy between the elements from lithium to fluorine compared with those from sodium to chlorine.

The oxygen compounds exhibit a regularly increasing capacity of the elements for oxygen from lithium to nitrogen, and again from sodium to sulphur. The first four oxides in each column are analogous to the first four chlorides or hydrides, one atom of oxygen being equivalent to two of chlorine or of hydrogen. Such of the remaining elements in the table as form oxides possess a greater capacity for oxygen than for hydrogen or chlorine.

When we compare the hydroxides, a gradation in properties is also striking. The hydroxides which form the most familiar salts answer our purpose best. They are

LiOH	NaOH
$Be(OH)_2$	$Mg(OH)_2$
$B(OH)_3$	$Al(OH)_3$
$CO(OH)_2$	$SiO(OH)_2$ and $Si(OH)_4$
NO_2OH	PO_2OH and $PO(OH)_3$
——	$SO_2(OH)_2$
——	ClO_3OH

Lithium hydroxide is a strong base ; beryllium hydroxide is also a base, but may be separated from salts by lithium hydroxide ; boron hydroxide possesses no basic properties, but is a feeble acid, displaced by even carbonic acid ; carbon hydroxide is never basic, and is set free by the common strong acids ; the hydroxide of nitrogen is nitric acid ; fluorine forms no hydroxide or oxy-acid. Following next is sodium hydroxide, a strong base like lithium hydroxide ; magnesium hydroxide is a weaker base ; aluminum hydroxide is a still weaker base, and also possessing slightly acidic properties ; silicon hydroxide is never basic, and is displaced by stronger acids ; and the hydroxides of phosphorus, sulphur, and chlorine are powerful acids.

The elements from lithium to fluorine exhibit a regular gradation from strongly basic to strongly acidic characteristics ; and the same holds good from sodium to chlorine. The elements we have considered belong to the first period of Mendelejeff's classification. A careful study of the members of the second and third periods will make evident a similar variation in properties from element to element, with a return to very like properties at certain fixed points. This leads to the hypothesis that the chemical properties of an element are very largely determined by its atomic weight. It may be stated that physical properties, e.g., melting and boiling points, densities, and atomic volumes, bear a relation to, and to a greater or less degree are dependent upon, the atomic weights.

The Periodic Law.—*The properties of the elements vary from member to member in order of increasing atomic weights, and return to more or less closely related properties at fixed points in the whole series of the elements; and certain properties appear periodically.*

The classification makes evident the meaning of this law. Periodicity appears in the elements of any group, e.g., in case of the closely allied metals of the first group, or the halogens of the seventh group. Further, we see that in regard to valence there is an increase from the first to the seventh group, and in a less marked degree to the eighth group. Since the valence which an element exhibits depends upon the compound containing it, and is a variable property, it must be borne in mind that while there is evidently a periodicity in valence, there are some exceptions to the rule that the highest valence of an element corresponds to the number of the group in which the element falls. This is, to a degree, connected with the fact that members of one group possess certain properties in common with some members of another group. Lithium in the insolubility of its carbonate and phosphate resembles magnesium. Copper in its more stable compounds is bivalent, and its more common salts are analogous to the salts of the members of the second group. Gold in its trivalent character is allied to the third group. Thallium in thallous compounds resembles the alkali metals. Lead, which is tetravalent, forms salts analogous in formula to the salts of the members of the second group; its sulphate is insoluble like the sulphates of calcium, strontium, and barium. The members of the fifth group in their trivalent character resemble the elements of the third group; iron in ferrous compounds is related to the second group, and in ferric compounds to the third group. Numerous other examples might be stated.

The element having the lowest atomic weight stands apart from the other members of a group. This has been shown in the summaries of the groups, and need not here be illustrated by examples. In a group whose members falling in period I. are non-metals we find with increasing atomic weights that metallic and basic properties increase. For instance, phosphorus is a non-metal, and is only acidic ; arsenic is somewhat metallic in character, and feebly basic : and in antimony metallic and basic characters are more pronounced.

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